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RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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(Continued from p. 234.)

Twenty-atom Series.—The salts of this series closely resemble those which have been described. I did not succeed in preparing the acid, though I made repeated attempts to do so by mixing sodic tungstate and phosphate together in the proportion of 20 molecules of the former to 2 of the latter, neutralizing with nitric acid, precipitating by mercurous nitrate, and decomposing the mercurous salt by dilute chlorhydric acid. The acid formed always underwent partial decomposition upon concentration, a white crystalline powder being separated while the 24-atom acid was formed. The only well-defined salt of the series which I have obtained is the normal barium compound. From this it will doubtless be possible to obtain others by double decomposition.

Normal 20-atom Barium Salt.—As the baric phospho-tungstates crystallize in general much more readily than the corresponding sodic salts, I employed them to determine what compounds are formed when sodic tungstate and phosphate are mixed in various proportions. To solutions of the two salts in the ratios of 24 molecules of the former to 2 of the latter, of 18 to 2, and of 12 to 2, chlor-

hydric acid was added until the reaction became just distinctly acid. Baric chloride was then added in excess, and the solutions were quickly filtered from the insoluble white precipitate formed. Beautiful colorless crystals formed, which were readily soluble in hot water, and could be recrystallized without difficulty. These salts proved to have in all cases the same composition, and are represented by the formula

$$20\,WO_3\,.\,P_2O_5\,.\,6\,BaO+48\,aq,$$

as the following analyses show:

I.

1.1103 gr. lost on ignition with fused borax 0.1458 gr. = 13.14 per ct. water.
1.1831 gr. " " " " 0.1560 gr. = 13.18 per ct. "
1.0691 gr. gave 0.7775 gr. WO_3 and P_2O_5 = 72.72 per ct.
0.9390 gr. " 0.6850 gr. " = 72.84 per ct.

II.

1.0676 gr. lost on ignition 0.1400 gr. = 13.11 per ct. water.
0.6550 gr. gave 0.4763 gr. WO_3 and P_2O_5 = 72.72 per ct.

III.

1.1110 gr. lost on ignition 0.1461 gr. = 13.15 per ct. water.
0.6409 gr. gave 0.4667 gr. WO_3 and P_2O_5 = 72.81 per ct.
and 0.0704 gr. $P_2O_{11}U_2$ = 2.18 per ct. P_2O_5
0.6222 gr. gave 0.0710 gr. $P_2O_{11}U_2$ = 2.26 per ct. "

Analyses I were made with the salt from the 24 to 2; II from that obtained from the 12 to 2; and III from the salt of the 18 to 2 mixture. The phosphoric oxide was precipitated twice.

		Calc'd.	Mean.				
20 WO_3	4640	70.67	70.55	70.50	70.62	70.50	70.59
P_2O_5	142	2.17	2.22	....	....	....	2.18 2.26
6 BaO	918	13.99	14.09	....	....	....	....
48 H_2O	864	13.17	13.14	13.14	13.18	13.11	13.15
	6564	100.00	100.00				

The salt dissolves readily in hot water, giving a somewhat milky solution. Chlorhydric acid gives no precipitate at first, but after a time a white crystalline powder is formed, which is the acid salt of the 24-atom series already described.

The fact that the same salt is formed independently of the proportions of sodic tungstate and phosphate is an important one, and illustrates the peculiarities of the series of phospho-tungstates which I have already pointed out.

Eighteen-atom Series.—When normal sodic tungstate and hydrodisodic phosphate are dissolved together in the proportion of 20 molecules of the former to 2 of the latter, and acetic acid is added to the boiling solution until a distinctly acid reaction is obtained, alcohol in excess precipitates a white indistinctly crystalline salt. This dissolves very readily in water, but gives on evaporation a gummy mass, and distinct crystals cannot be obtained. The solution of this salt gives no precipitate at first with salts of potassium, but after a short time beautiful colorless crystals are formed in abundance. The salt dissolves in a rather large excess of water, leaving a small quantity of a white insoluble compound. It crystallizes best from a solution which is not very concentrated, and which is allowed to evaporate spontaneously in the air. The crystals obtained in this way are colorless and well-defined prisms. On re-solution it almost always leaves a small quantity of the slightly soluble salt; but when the whole is dissolved together, the more soluble compound crystallizes without perceptible admixture of the other. From very concentrated solutions I obtained a white granular salt, which, on re-solution in a rather large quantity of water, gave the colorless crystals again.

Of the colorless transparent crystals,

1.1470 gr. gave	0.9372 gr.	$WO_3+P_2O_5$	=81.71 per ct.
1.5149 gr. "	1.2387 gr.	"	=81.77 per ct.
1.3494 gr. lost	0.1089 gr.	water	= 8.07 per ct.
1.5806 gr. "	0.1277 gr.	"	= 8.08 per ct.
1.1391 gr. gave	0.0498 gr.	$Mg_2P_2O_7$	= 2.80 per ct. P_2O_5
1.1856 gr. "	0.0506 gr.	"	= 2.93 per ct. "
1.5149 gr. "	0.4738 gr.	AgCl	=10.26 per ct. potassium.

These analyses correspond to the formula

$$18\ WO_3\ .\ P_2O_5\ .\ 6\ K_2O+23\ aq.$$

which requires:

		Calc'd.	Mean.		
18 WO_3	4176	78.81	79.12	78.95	79.01
P_2O_5	142	2.68	2.62	2.65	2.58
6 K_2O	566.4	10.69	10.24	....	....
31 H_2O	414	7.82	8.08	8.07	8.08
	5298.4	100.00			

Of the white granular hydrate,

1.3868 gr. gave	1.0985 gr. $WO_3+P_2O_5$=79.21 per ct.
0.9528 gr. "	0.7556 gr. " =79.30 per ct.
1.0396 gr. "	0.0409 gr. $P_2O_7Mg_2$ = 2.57 per ct. P_2O_5
1.0614 gr. "	0.0425 gr. " = 2.56 per ct. "
1.0102 gr. lost on ignition	0.1009 gr. water = 9.99 per ct.
1.7974 gr. "	0.1800 gr. " =10.01 per ct.

The corresponding formula is

$$18\ WO_3 . P_2O_5 . 6\ K_2O + 30\ aq,$$

which requires:

		Calc'd.	Mean.		
18 WO_3	4176	76.98	76.84	76.89	76.80
P_2O_5	142	2.62	2.42	2.41	2.42
6 K_2O	566.4	10.44	10.74	....	....
30 H_2O	540	9.96	10.00	9.99	10.01
	5424.4	100.00			

The prismatic and granular salts, therefore, only differ in water of crystallization. It must be remarked, however, that the corrected percentages of the phosphoric oxide in the analyses of the granular salt are too low, which is unusual.

18 : 1 Acid Potassium Salt.—When the normal salt is dissolved in water and chlorhydric acid is added in excess, a white crystalline precipitate is formed, which is but very sparingly soluble in water. Of this salt,

1.2955 gr. gave	1.1828 gr. $WO_3 + P_2O_5$=91.30 per ct.
1.3200 gr. "	1.1994 gr. " =90.86 per ct.
1.1390 gr. "	0.0592 gr. $P_2O_7Mg_2$ = 3.32 per ct. P_2O_5
1.5900 gr. "	0.0817 gr. " = 3.29 per ct. "
1.5225 gr. lost on ignition	0.1087 gr. water = 7.14 per ct.
1.1966 gr. " "	0.0856 gr. " = 7.16 per ct.

These analyses correspond to the formula

$$18\ WO_3 . P_2O_5 . K_2O . 5\ H_2O + 14\ aq.$$

		Calc'd.	Mean.		
18 WO_3	4176	87.84	87.93	88.15	87.71
P_2O_5	142	2.99	3.15	3.17	3.14 corrected.
K_2O	94.4	1.98	1.77	....	....
19 H_2O	342	7.19	7.15	7.16	7.14
	4754.4	100.00	100.00		

Ammonium Salt.—The ammonium salt of the 18-atom series may be prepared in the manner given above for the normal potassic compound. When ammonic acetate and alcohol are mixed with a

concentrated solution of the sodium salt, no precipitate is formed at first, but after some hours a mass of white crystals is thrown down. After washing with alcohol and re-solution, crystals may sometimes be obtained, but the salt usually forms a nearly colorless gummy mass. In this case white opaque crystals separate from a thick and syrupy mother-liquor. The crystals are soft and gummy to the touch. I did not succeed in obtaining the salt in a state of purity suitable for analysis.

Sixteen-atom Series.—The only representatives of this series which I have obtained are salts of calcium, potassium, and ammonium. They are all well defined and more or less distinctly crystalline.

16 : 1 Acid Calcium Salt.—When calcic tungstate, WO_4Ca, is boiled with a pure dilute solution of phosphoric acid, the salt is dissolved very slowly; but on addition of a few drops of chlorhydric acid, the tungstate passes quickly into solution. The liquid deposits on evaporation colorless, flat, tabular crystals readily soluble in water. Of these crystals,

{ 0.7356 gr. gave	0.6992 gr. $WO_3+P_2O_5$=95.05 per ct.
{ 0.7356 gr. "	0.0390 gr. $P_2O_7Mg_2$ = 3.39 per ct. P_2O_5
1.0347 gr. lost on ignition	0.0366 gr. water = 3.54 per ct.

The phosphoric acid was twice precipitated. The analyses lead to the formula

$$16\ WO_3 . P_2O_5 . CaO . 5\ H_2O + 3\ aq,$$

which requires:

		Calc'd.	
16 WO_3	3712	91.56	91.66
P_2O_5	142	3.50	3.39
CaO	56	1.38	1.41 (diff.)
8 H_2O	144	3.56	3.54
	4054	100.00	

16 : 4 Acid Potassium Salt.—In the attempt to prepare the sodium salt to which Scheibler gave provisionally the formula

$$Na_8H_{11}W_8P_2O_{31}+13\ aq,$$

I obtained a thick syrupy liquid, which on dilution with water gave with potassic bromide, after standing a few hours, beautiful colorless needles. The salt is readily soluble in hot water. After recrystallization,

0.5991 gr. gave	0.5000 gr. $WO_3+P_2O_5$=83.46 per ct.	
2.1547 gr. "	0.1005 gr. $P_2O_7Mg_2$	= 2.98 per ct. P_2O_5
1.0492 gr. lost on ignition	0.0841 gr. water	= 8.01 per ct.

The analyses gave the formula

$$16\ WO_3 . P_2O_5 . 4\ K_2O . 2\ H_2O + 19\ aq,$$

or,

$$W_{16}P_2O_{47}(KO)_8(HO)_4 + 19\ aq,$$

which requires :

		Calc'd.	
16 WO_3	3712	80.53	80.48
P_2O_5	142	3.08	2.98
4 K_2O	377.6	8.19	8.53 (diff.)
21 H_2O	378	8.20	8.01
	4609.6	100.00	

16 : 6 Ammonium Salt.—This beautiful salt was prepared by adding a solution of ammonic chloride to the syrupy liquid obtained by boiling 12:5 sodic tungstate with half its weight of a strong solution of pure phosphoric acid. After standing 12 hours an abundant precipitate of the ammonium salt was formed. This precipitate, after being well drained and twice recrystallized, gave very fine flat prismatic crystals. It is the best-defined ammonium salt which I have obtained. The salt is readily soluble in hot water, and crystallizes as the solution cools. Of this salt,

1.4108 gr. lost on ignition	0.1627 gr. $H_2O + NH_3$	= 11.58 per ct.
0.7705 gr. " "	0.0886 gr. "	= 11.49 per ct.
0.7705 gr. gave	0.1243 gr. $P_2O_{11}U_2$	= 3.21 per ct. P_2O_5
0.9629 gr. "	0.1430 gr. NH_4Cl	= 7.17 per ct. $(NH_4)_2O$.

The analyses correspond with the formula

$$16\ WO_3 . P_2O_5 . 6\ (NH_4)_2O + 10\ aq,$$

which requires :

		Calc'd.	Mean.		
16 WO_3	3712	85.41	85.28	85.30	85.26
P_2O_5	142	3.27	3.21	.... 3.21	....
6 $(NH_4)_2O$	312	7.18	7.17	.... 7.17	....
10 H_2O	180	4.14	4.34	4.32	4.36
	4346	100.00	100.00		

14 : 2 Series.—The only compound of this series which I have obtained is a sodium salt with the empirical formula

$$14\ WO_3 . 2\ P_2O_5 . 5\ Na_2O + 42\ aq.$$

I regard this as a double salt, or perhaps as a compound of an 8-atom and a 6-atom salt.

14 : 5 Sodium Salt.—In the communication already referred to,* Scheibler described briefly a sodium salt to which he gave provisionally the formula

$$Na_8H_{11}P_2W_6O_{31}+13\ H_2O.$$

This salt was obtained by boiling 12 : 5 sodic tungstate with half its weight of phosphoric acid. After a short time the salt separates in beautiful crystals. As Scheibler's salt evidently belongs to a 6-atom series, and has therefore a special theoretical interest, I endeavored in various ways to prepare it, but in all cases without success. By boiling 12 : 5 sodic tungstate with half its weight of phosphoric acid I obtained a thick syrupy liquid, which after long standing gave crystals. In another experiment about 75 gr. of the sodium salt were boiled with 13 gr. of syrupy pure phosphoric acid. After dilution and standing for some days, splendid colorless prismatic crystals separated, identical in appearance with those of the last experiment. These were redissolved and recrystallized several times. Of this salt,

0.5551 gr. gave		0.4272 gr. $WO_3+P_2O_5$	=76.95 per ct.
0.5787 gr. "		0.4459 gr. "	=77.06 per ct.
1.5430 gr. "		1.1884 gr. "	=77.02 per ct.
1.0058 gr. "		0.0980 gr. $P_2O_7Mg_2$	= 6.35 per ct. P_2O_5
1.0285 gr. "		0.1014 gr. "	= 6.34 per ct. "
1.0023 gr. "		0.3214 gr. $P_2O_{11}U_2$	= 6.38 per ct. "
1.0152 gr. lost on ignition		0.1656 gr. water	=16.31 per ct.
1.0240 gr. "	"	0.1677 gr. "	=16.37 per ct.
0.9922 gr. "	"	0.1612 gr. "	=16.24 per ct.

These analyses correspond fairly well to the formula

$$14\ WO_3 . 2\ P_2O_5 . 5\ Na_2O+42\ aq,$$

which requires:

		Calc'd.	Mean.			
14 WO_3	3248	70.64	70.65	70.59	70.70	70.66
2 P_2O_5	284	6.18	6.36	6.35	6.34	6.38
5 Na_2O	310	6.74	6.65	....	....	....
42 H_2O	756	16.44	16.34	16.31	16.37	16.34
	4598	100.00				

The phosphoric oxide, which was twice precipitated, is too high, but it may be that in such salts a third precipitation is necessary to effect a perfect separation. I should write the formula of the salt, provisionally, either

* Berichte der deutschen chemischen Gesellschaft, 5, 801.

$$6\ WO_3 . P_2O_5 . 3\ Na_2O . 3\ H_2O + 8\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O + 35\ aq.$$

or

$$6\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O + 8\ WO_3 . P_2O_5 . 3\ Na_2O . 3\ H_2O + 35\ aq.$$

There appears to be no reason for distributing the sodic oxide in one way rather than in the other. On the other hand, it is perhaps equally probable that the salt is a compound of two acid salts of a 7-atom series, and that its formula is

$$7\ WO_3 . P_2O_5 . 3\ Na_2O . 3\ H_2O + 7\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O + 35\ aq.$$

Among the corresponding phospho-molybdates there is at least one series in which the number of atoms of the teroxide is odd. Potassium and ammonium salts in this series have respectively the formulas

$$5\ MoO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O + 4\ aq,$$
$$5\ MoO_3 . P_2O_5 . 3\ (NH_4)_2O . 3\ H_2O + 4\ aq,$$

if, provisionally, we consider the acid as 12-basic. With respect to the formula given above, and which is that of an acid double salt, I may remark that I shall describe farther on a salt of the 5-atom molybdenum series with the formula

$$5\ MoO_3 . P_2O_5 . 3\ (NH_4)_2O . 3\ H_2O + 5\ MoO_3 . P_2O_5 . 2\ (NH_4)_2O . 4\ H_2O,$$

and that Rammelsberg has already described the corresponding potassium compound. From the general analogy between tungsten and molybdenum, the existence of phospho-tungstates with an uneven number of atoms of tungstic oxide may be fairly inferred from that of phospho-molybdates of the type of the 5-atom compounds above mentioned. I must leave the question undecided, for the present at least, as I have not succeeded in obtaining corresponding salts of potassium, ammonium, strontium or calcium.

The salt crystallizes in long, flat, prismatic forms, and appears to be perfectly homogeneous, so that I believe it should be regarded as a definite compound, and not as a mixture. It is very soluble in water, and crystallizes only from syrupy solutions. It has a strongly marked sweet taste, which is at the same time astringent and very slightly bitter. The solution of the sodium salt gives with potassic bromide a beautiful crystalline precipitate, already described, and having the formula

$$16\ WO_3 . P_2O_5 . 4\ K_2O . 2\ H_2O + 19\ aq,$$

and with ammonic chloride, the ammonium salt

$$16\ WO_3 . P_2O_5 . 6\ (NH_4)_2O + 10\ aq,$$

also noticed above.

I endeavored to obtain the normal 6-atom sodium salt $6\,WO_3 . P_2O_5 . 6\,Na_2O$ by boiling six atoms of neutral sodic tungstate with the calculated quantity of pure phosphoric acid, but the experiment was unsuccessful.

When a solution of hydro-disodic phosphate is heated, and freshly prepared tungstic oxide is added, in small portions at a time, the oxide is readily dissolved with formation of a colorless or faintly bluish liquid. The solution gave crystalline precipitates with baric chloride and argentic nitrate, but the salts formed proved on analysis to be only mixtures. An ammonium salt was prepared by adding ammonic nitrate and nitric acid to the solution of the sodium salt. The ratio of tungstic to phosphoric oxide in the white crystalline salt formed was as 20 : 1 very closely; but this does not lead to any inference as to the formula of the sodium salt in solution. Tribasic sodic phosphate also dissolves tungstic oxide readily, and the same is true as regards ammonic phosphate; but I could not obtain definite salts from either solution. Potassic phosphate dissolves tungstic oxide very slowly, and only by long boiling. No definite compound was formed in this case.

When hydro-disodic phosphate and tungstic oxide are fused together the latter dissolves and forms a colorless fused mass. This is soluble in water, but, as in the other cases, gives no single well-defined salt. I have made no experiment to determine whether phospho-tungstates of the lower orders dissolve freshly precipitated tungstic oxide so as to form the higher terms in the series. The extraordinary amount of time and labor which I have already spent upon the subject must be my excuse for leaving this and many other interesting points to other investigators. There is no part of the subject which will not amply repay a new and careful study.

Arsenio-Tungstates.

When solutions of alkaline tungstates and arsenates are mixed it frequently happens that white crystalline precipitates are formed, the supernatant liquid becoming strongly alkaline. These precipitates are arsenio-tungstates, and, as might be expected, correspond in a general way to the class of phospho-tungstates already described. They appear to be as a rule less well defined than these last, and, so far as I have been able to discover, exhibit no character of special interest. In analyzing the few salts of this series

which I have studied, I have employed the same methods which I have used for the analysis of the phospho-tungstates. Only the conditions are necessarily in some respects different. Arsenic and tungstic oxides were precipitated together by mercurous nitrate, mercuric oxide being employed to secure perfect neutrality. The mercurous salt was then separated upon an asbestos filter, and, after drying, ignited—finally with the blast-lamp—until a constant weight was obtained. In this manner very nearly the whole of the arsenic oxide was volatilized. There is no danger of a reduction to metallic arsenic if the crucible containing the asbestos and precipitate is placed within another, covered, and then cautiously heated. The arsenic oxide is best determined as ammonio-magnesic arsenate, using a large excess of magnesia-mixture in the first precipitation. Two precipitations are necessary to secure a perfect separation; the salt is to be collected on an asbestos filter, and dried in the usual manner. In determining water, or water and ammonia, in these salts, it is best to ignite with a weighed quantity of fused sodic tungstate, as suggested to me by Dr. Gooch; only it must be observed that the fused tungstate is rather deliquescent. With all these precautions fairly good results may be obtained. I endeavored to separate arsenic from tungstic oxide by boiling the salt with dilute phosphoric acid, reducing the arsenic to arsenous acid by sulphurous acid, and then precipitating by sulphydric acid as As_2S_3. This method appears to give a complete separation, but is very tedious and circumstantial.

Acid 3-atom Potassic Arsenio-tungstate.— When 12 : 5 acid potassic tungstate is dissolved, and a solution of potassic arsenate, AsO_4KH_2, is added, a white, very fine-grained precipitate is formed. When an excess of the arsenate is employed, and the mixed solutions are evaporated upon a water-bath, a perfectly white insoluble salt is separated, which is the acid arsenio-tungstate

$$6\,WO_3 . As_2O_5 . 3\,K_2O . 3\,H_2O.$$

The formation of this salt may be represented by the equation

$$12\,WO_3 . 5\,K_2O + As_2O_5 . K_2O . 2\,H_2O + 4\,H_2O = 2\{6\,WO_3 . As_2O_5 . 3\,K_2O . 3\,H_2O\}.$$

For analysis the salt was washed upon a filter with hot water, then dried upon paper, and afterward—as the mass remained pasty—upon a water-bath, where it finally dried to a hard white mass. Of this salt,

0.8276 gr. gave 0.5902 gr. WO_3 = 71.31 per ct.
0.7197 gr. " 0.5130 gr. " = 71.28 per ct.
1.9815 gr. " 0.3841 gr. $As_2O_5Mg_2(NH_4)_2+H_2O$ = 11.73 per ct. As_2O_5
1.3507 gr. lost on ignition 0.0357 gr. water = 2.64 per ct.

The formula requires:

		Calc'd.		
6 WO_3	1392	71.05	71.31	71.28
As_2O_5	230	11.75		11.73
3 K_2O	283	14.45		14.33 (diff.)
3 H_2O	54	2.75		2.64
	19.59	100.00		

The salt dissolves readily in alkaline hydrates. Its chief interest lies in the fact that it serves to establish the existence of a 6-atom series of arsenio-tungstates.

Acid 6 : 4 Ammonium Salt.—When ammonic arsenate AsO_4NH_4 and neutral sodic tungstate are dissolved together, no precipitate is formed at first, but after a short time a dense white crystalline salt is thrown down, which after twelve hours becomes abundant. Boiling water dissolves this salt readily, but it does not crystallize well from the solution, forming only a thick white mass. If this mass be dissolved in water, nitric acid added in excess gives a white crystalline precipitate, but slightly soluble in the acid liquid and in water. Of this salt, after washing with cold water,

0.8255 gr. gave 0.6013 gr. WO_3 = 72.84 per ct.
1.9486 gr. " 0.3980 gr. $As_2O_5Mg_2(NH_4)_2 + H_2O$ = 12.36 per ct. As_2O_5
1.2494 gr. " 0.2635 gr. NH_4Cl = 10.25 per ct.

The analyses agree, though not very closely, with the formula

$$6\ WO_3 . As_2O_5 . 4\ (NH_4)_2O . 2\ H_2O + 3\ aq.$$

which requires:

		Calc'd.	
6 WO_3	1392	72.50	72.84
As_2O_5	230	11.98	12.36
4 $(NH_4)_2O$	208	10.83	10.25
5 H_2O	90	4.69	4.55 (diff.)
	1920	100.00	

The differences are, I think, not greater than may be expected in cases in which the salt analyzed cannot be purified by recrystallization.

Normal 16 : 6 Silver Salt.—I obtained this salt by the following process: 100 gr. neutral sodic tungstate and 25 gr. arsenic acid were dissolved together and the solution boiled for some time, then filtered and evaporated upon a water-bath. After a day much sodic arsenate separated in crystals. The filtrate from these crystals deposited a white indistinctly crystalline mass. This was redissolved and potassic bromide added in excess, when an abundant white crystalline fine-grained precipitate was thrown down, which was drained on the filter-pump, and then washed with cold water. This was dissolved in much boiling water, and argentic nitrate added, when a white crystalline salt was thrown down mixed with brownish-red crystals of argentic arsenate. The mass was treated with very dilute nitric acid, which readily dissolved the arsenate, the undissolved portion appearing under a lens as made up of opaque, white, acicular crystals. These were well drained, washed with cold water, and dried on paper by pressure, when the mass showed a faint yellowish tint. The salt is but slightly soluble in cold water. Of this salt,

0.7488 gr. gave	0.5024 gr. WO_3	= 67.09 per ct.
0.7531 gr. "	0.5067 gr. "	= 67.29 per ct.
2.0321 gr. "	0.6147 gr. AgCl	= 24.45 per ct. Ag_2O
1.0215 gr. "	0.3096 gr. "	= 24.48 per ct. "
0.9209 gr. lost on ignition	0.0340 gr. water	= 3.69 per ct.

The analyses correspond tolerably well to the formula

$$16\ WO_3\ .\ As_2O_5\ .\ 6\ Ag_2O + 11\ aq,$$

which requires:

		Calc'd.	
16 WO_3	3712	67.10	67.09 .... 67.29
As_2O_5	230	4.16	.... 4.65 (diff.)
6 Ag_2O	1392	25.16	24.45 .... 24.48
11 H_2O	198	3.58	.... 3.69 ....
	5532	100.00	

I do not place implicit confidence in the formula given, as the two determinations of argentic oxide are too low. It is very possible that the salt was slightly decomposed by the dilute nitric acid employed to remove the arsenate. But in any case it is proved that arsenio-tungstates exist in which the ratio of WO_3 to As_2O_5 is higher than 6 : 1, and a method of obtaining such compounds is pointed out.

General Conclusions.—The general results of my investigation of the phospho-tungstates may be stated briefly as follows:—

1. The phospho-tungstates form a series of which the lowest term probably contains six atoms of tungstic to one of phosphoric oxide, and the highest, twenty-four atoms of tungstic to one of phosphoric oxide.

2. At least the greater number of phospho-tungstates contain an even number of atoms of tungstic oxide. The homologizing term for these cases is therefore $2\,WO_3$.

3. The highest number of atoms of base observed in any case is six (old style), which implies that the acid contains twelve atoms of hydroxyl.

4. In all cases observed the number of atoms of hydroxyl replaced by a monatomic metal is even.

5. One instance occurs in which two acid phospho-tungstates of different orders appear to unite to form a definite compound; but this case admits of a different explanation.

6. In all phospho-tungstates studied the number of atoms of base or of hydroxyl is more than sufficient to saturate the phosphoric oxide present, if we admit that the acid is 12-basic. At least a part of the hydroxyl or base must therefore be united to tungstic oxide.

For greater facility of comparison I have brought together the formulas of all the compounds described in this paper, writing them both with the old and the new notation.

$24\,WO_3 . P_2O_5 . 6\,H_2O + 47$ aq	$W_{24}P_2O_{71}(HO)_{12} + 47$ aq
$24\,WO_3 . P_2O_5 . 6\,H_2O + 34$ aq	$W_{24}P_2O_{71}(HO)_{12} + 34$ aq
$24\,WO_3 . P_2O_5 . 6\,H_2O + 55$ aq	$W_{24}P_2O_{71}(HO)_{12} + 55$ aq
$24\,WO_3 . P_2O_5 . 2\,Na_2O . 4\,H_2O + 23$ aq	$W_{24}P_2O_{71}(NaO)_4(HO)_8 + 23$ aq
$24\,WO_3 . P_2O_5 . 3\,K_2O . 3\,H_2O + 8$ aq	$W_{24}P_2O_{71}(KO)_6(HO)_6 + 8$ aq
$24\,WO_3 . P_2O_5 . 3\,K_2O . 3\,H_2O + 14$ aq	$W_{24}P_2O_{71}(KO)_6(HO)_6 + 14$ aq
$24\,WO_3 . P_2O_5 . 3\,(NH_4)_2O . 3\,H_2O + 26$ aq	$W_{24}P_2O_{71}(NH_4O)_6(HO)_6 + 26$ aq
$24\,WO_3 . P_2O_5 . 3\,BaO . 3\,H_2O + 43$ aq	$W_{24}P_2O_{71}(BaO_2)_5(HO)_8 + 43$ aq
$22\,WO_3 . P_2O_5 . 2\,K_2O . 4\,H_2O + 2$ aq	$W_{22}P_2O_{65}(KO)_4(HO)_8 + 2$ aq
$22\,WO_3 . P_2O_5 . 3\,(NH_4)_2O . 3\,H_2O + 18$ aq	$W_{22}P_2O_{65}(NH_4O)_6(HO)_6 + 18$ aq
$22\,WO_3 . P_2O_5 . 2\,Na_2O . 4\,H_2O + 5$ aq	$W_{22}P_2O_{65}(NaO)_4(HO)_8 + 5$ aq
$22\,WO_3 . P_2O_5 . 4\,BaO . 2\,H_2O + 39$ aq	$W_{22}P_2O_{65}(BaO_2)_4(HO)_4 + 39$ aq
$20\,WO_3 . P_2O_5 . 6\,BaO + 48$ aq	$W_{20}P_2O_{59}(BaO_2)_6 + 48$ aq
$18\,WO_3 . P_2O_5 . 6\,K_2O + 23$ aq	$W_{18}P_2O_{53}(KO)_{12} + 23$ aq
$18\,WO_3 . P_2O_5 . 6\,K_2O + 30$ aq	$W_{18}P_2O_{53}(KO)_{12} + 30$ aq
$18\,WO_3 . P_2O_5 . K_2O . 5\,H_2O + 14$ aq	$W_{18}P_2O_{53}(KO)_2(HO)_{10} + 14$ aq

16 $WO_3 . P_2O_5 . CaO . 5\ H_2O + 3$ aq	$W_{16}P_2O_{47}(CaO_2)(HO)_{10} + 3$ aq
16 $WO_3 . P_2O_5 . 4\ K_2O . 2\ H_2O + 19$ aq	$W_{16}P_2O_{47}(KO)_8(HO)_4 + 19$ aq
16 $WO_3 . P_2O_5 . 6\ (NH_4)_2O + 10$ aq	$W_{16}P_2O_{47}(NH_4O)_{12} + 10$ aq
14 $WO_3 . 2\ P_2O_5 . 5\ Na_2O + 42$ aq	
6 $WO_3 . As_2O_5 . 3\ K_2O . 3\ H_2O$	$W_6As_2O_{27}(KO)_6(HO)_6$
6 $WO_3 . As_2O_5 . 4\ (NH_4)_2O . 2\ H_2O + 3$ aq	$W_6As_2O_{27}(NH_4O)_8(HO)_4 + 3$ aq
16 $WO_3 . As_2O_5 . 6\ Ag_2O + 11$ aq	$W_{16}As_2O_{47}(AgO)_{12} + 11$ aq

In writing these formulas I have assumed that *all* the acids are 12-basic, since it has been shown that there are salts of the sixteen, eighteen and twenty-atom series which correspond with this view. I shall resume the discussion of the subject in connection with the phospho-molybdates, and at the same time examine in detail the question of the existence of a distinct class of pyro-salts of the tungstic and molybdic series.

(*To be continued.*)

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.

ESTIMATION OF ALKALOIDS BY POTASSIUM MERCURIC IODIDE.

By Albert B. Prescott.

In 1862, Ferdinand F. Mayer, of New York, reported* the uses of a standard solution of mercuric iodide with excess of potassium iodide, in a method of volumetric determination of the chief natural alkaloids. The standard solution was a "decinormal," or, taking Hg at 200, a twentieth normal solution of ($HgCl_2 + 6KI$), and has been generally known as Mayer's solution, in use for qualitative as well as quantitative purposes. Mr. Mayer so far extended his investigation that, for twelve alkaloids, he stated the number of milligrams of alkaloid precipitated by a cubic centimeter of his standard solution. These volumetric factors coincided with mole-

* Pro. Am. Phar. Asso. 1862, 238; and again, more fully, Chem. News. 7, 159. April 4, 1863, and, on opium alkaloids, Ibid. 8, 177, 189, Oct. 10, 17, 1863. Am. Jour. Phar. 35, 20. Zeitsch. an. Chemie, 2, 225 (1863). Jahresbericht der Chemie, 1863, 703.

cular quantities, proposed by theory and approved by experiment. The stated quantity of each alkaloid represented its equivalent weight, or the half its equivalent weight, or the whole or the third of twice its equivalent weight. The general correctness of the factors declared by Mayer has obtained frequent confirmation, though, as will be specified further on, some of his numbers have been found to require adjustment, irrespective of molecular quantities, and the combining numbers of some of the alkaloids of his list have become unsettled. Moreover, it has been found that the proportion of alkaloid to iodomercurate is in many cases varied by conditions, so that limits of dilution, time, temperature, etc., need to be prescribed. As a working process there still lacks an indicator for the end of the reaction,—one recommended by Mr. Mayer being palpably fallacious. Another demand for more investigation of the subject lies in apparent discrepancies between the volumetric factors of precipitation and some gravimetric analyses of the precipitates. Upon several of these questions I have at various times obtained some work, reaching as yet few conclusive results, but which may serve even now, with a careful study, to put the subject and its deficiencies in a more tangible shape.

A few years before Mr. Mayer's report, Thomas B. Groves, of Weymouth, England, communicated an investigation "On Some Compounds of Iodide and Bromide of Mercury with the Alkaloids."* Mr. Groves obtained his compounds by precipitation with "a solution of three equivalents of iodide or bromide of potassium, and one equivalent of chloride of mercury" [Hg=100], that is, the constituents of the reagent afterward standardized for volumetric use by Mr. Mayer. Mr. Groves introduces the alkaloidal mercuric iodides, etc., as a class of compounds which he believes has not hitherto been noticed, but in fact the qualitative reaction of alkaloids with solution of iodide of mercury and potassium had been communicated some time before. It is referred to in Gmelin's Hand-book, among the combinations of metallic iodides.† A. von Planta-Reichenau, in a good compilation on the reactions of alkaloids, presented as a dissertation at Heidelberg‡ in 1846, accords potassium mercuric iodide a prominent place among the general

*Quar. Jour. Chem. Soc. 11, 97, 188 (1859). Phar. Jour. Trans. 18, 181. Jahresbericht der Chemie, 1858, 363. Am. Jour. Phar. 36, 535.

†Cavendish Edition, 2 (1849), 184.

‡Das Verhalten der wichtigsten Alkaloide gegen Reagentien, S. 41.

reagents for these bases. Mayer credits the first report of the use of potassium mercuric iodide as a qualitative reagent for alkaloids to F. L. Winckler, in 1830.

Mr. Groves made precipitates from solutions of "one equivalent of alkaloid," in salt and with some excess of mineral acid, and "three equivalents of iodide (or bromide) of potassium" with "one equivalent of chloride of mercury," and then made quantitative determinations of the mercury and the iodine of these precipitates. In these analyses, a dried and weighed portion of the [washed] precipitate was dissolved in boiling alcohol, and the solution treated with an excess of fresh ammonium sulphide, to precipitate the mercury as sulphide. The solution was kept hot, slightly acidulated with nitric acid, and the mercuric sulphide separated and weighed. The filtrate was warmed to expel all hydrogen sulphide, and treated with solution of silver nitrate, for the gravimetric determination of the iodine. The difference was estimated as alkaloid. Mr. Groves reported the precipitates as perfectly crystallizable, from hot water or hot alcohol, but did not take the crystalline form for analysis. He made analyses of the precipitates of morphine, strychnine, quinine, and cinchonine. In duplicate operations the results agreed with each other fairly, the variations of iodine percentage being from 0.17 per cent. to 0.82 per cent. of the compound. The results are given in support of the general formula (translating Hg to 200), $AlkHgI_3$. This would be generally referred to the rational form, $AlkHIHgI_2$. However, the formula is not very well supported by the results. By computing the percentages of alkaloids for Mr. Groves' formulae, we obtain:

		Calculated.	Found.
Morphine in	$C_{17}H_{19}NO_3HgI_3$,	32.91	35.99 mean, from 35.97 and 36.02
Strychnine in	$C_{21}H_{22}N_2O_2HgI_3$,	36.50	33.03 " 33.20 " 32.87
Quinine in	$C_{20}H_{24}N_2O_2HgI_3$,	35.80	30.14 " 30.40 " 29.88
Cinchonine in	$C_{20}H_{24}N_2OHgI_3$,	34.64	29.08 " 28.56 " 29.60

Mr. Groves remarks that the obtained percentages of quinine and cinchonine correspond to molecular weights one-fourth less than those received.

A few months ago I obtained some determinations, by Messrs. FRANK E. JUDSON and CHARLES E. PAYNE, of the percentages of iodine and mercury, in the iodomercurates of several alkaloids, namely: strychnine, morphine, quinine and berberine. The ana-

lyses were done a little differently from those by Mr. Groves. The alkaloid precipitate was dried at 100° C., and a weighed portion dissolved in hot alcohol. It was found that the strychnine precipitate could be dissolved by acidulating the hot alcohol with sulphuric acid. Nitrate of silver solution was then added to precipitate the iodine, and the precipitate washed on the filter with hot water (dissolving out any silver sulphate precipitated by the alcohol), dried at 100° C., and weighed. The filtrate was treated with hydrochloric acid (in but slight excess), and the silver chloride filtered out, when this filtrate was charged with washed hydrogen sulphide gas, and the resulting mercury sulphide washed, dried at 100° C., and weighed. Having the iodine and the mercury, the fraction of hydrogen for the HI of the assumed formula was added, and the difference placed as alkaloid. Triplicate operations were made. The analysis of *the strychnine precipitate* gave the following results, placed parallel with centessimals calculated from a molecular formula, and with the mean of Groves' percentages:

	Calculated from		Judson & Payne.				Groves.
	$C_{21}H_{22}N_2O_2HIHgI_2$.		1st.	2d.	3d.	Mean.	Mean.
Iodine	381	41.59	40.70	40.69	40.00	40.46	44.19
Mercury	200	21.83	18.50	19.60	21.20	19.77	22.78
H of HI	1	00.11	...	...	...	00.11	...
Strychnine	334	36.47	...	...	...	39.66	33.03
	916	100.00				100.00	100.00

These results, in absence of direct determinations of the alkaloid raise the question whether the iodomercurate of strychnine, as a precipitate, may not be in some degree complex and variable. This precipitate is one of the least soluble of the iodomercurates, according to Mayer, being obtained in a solution containing 1-150,000th of strychnine. The end of the reaction is distinct, and the precipitate settles fairly in acidulated water, but better in concentrated solution of potassium chloride.* In this solution, Dragendorff found each cc. to dissolve 0.00216 gram of the precipitate. Without potassium chloride, 0.1127 gram of strychnine lost 0.0021 gram in precipitating, washing, and estimating from the formula above assumed.† From these gravimetric experiments it

* Dragendorff: Werthbestimmung starkwirkender Droguen (1874), 62, 69.

† Ibid. p. 68. Strychnine 0.1127 gram, with 7.5 cc. of Mayer's solution (an excess of 0.8 cc.), gave a precipitate of 0.3033 gram. Then $0.3033 \times 36.47 = 0.1106$, strychnine obtained.

appears that the precipitate in question must consist mainly, and may consist wholly of double iodide of the formula

$$C_{21}H_{22}N_2O_2HIHgI_2.$$

The volumetric factor of 0.0167 gram strychnine ($\frac{334}{1000}$ of $C_{21}H_{22}N_2O_2$ in grams), for 1 cc. Mayer's solution (containing $\frac{1000}{1000}$ of HgI_2+4KI in grams), is well established. I have several times obtained its verification with pure crystallized alkaloid. Dragendorff quotes experiments confirming the ratio.* Now our understanding of the chemical equation, in the formation of these alkaloid iodomercurates, must depend upon the composition of the precipitate, as we have little knowledge of the chemical composition of potassium mercuric iodide solutions. As a proposition, we may take this equation:

$$(C_{21}H_{22}N_2O_2)_2H_2SO_4+2(KIHgI_2+3KI)=$$
$$2C_{21}H_{22}N_2O_2HIHgI_2+K_2SO_4+6KI.$$

This presupposes the following formation of Mayer's solution:

$$HgCl_2+6KI=KIHgI_2+3KI+2KCl.$$

The conditions of mixture of Mayer's solution seem to deny that it holds three molecules of *free* potassium iodide (as we have to specify, further on). Nevertheless, some experiments in support of the above equations may be cited. A certain quantity (varied by temperature) of mercuric chloride may be added to Mayer's solution before a permanent red precipitate is attained. If, now, the solution just saturated with mercuric chloride, and containing the least perceptible precipitate of mercuric iodide, be treated with strychnine acidulated solution nearly to completion of the precipitate, and this be filtered out, the filtrate will not bear the least addition of mercuric chloride without production of a red precipitate of iodide of mercury. That is to say, all the iodide which is necessary to hold the mercuric iodide in solution, enters into the precipitate of alkaloid mercuric iodide. The indication is that none of the iodide belonging to the potassium mercuric iodide and essential to its solubility, becomes liberated in the precipitation with strychnine salt. These results are not peculiar to strychnine precipitation, as I obtained the same results with quinine, atropine and aconitine. Another test, implying that soluble iodide is not

* L. c. p. 62. Strychnine 0.0628 gram, in 10 cc. solution, with 5 cc. concentrated potassium chloride solution, required 3.75 cc. Mayer's solution, indicating 0.0626 strychnine.

liberated in the alkaloid iodomercurate precipitation, was made as follows: Mayer's solution was saturated with mercuric chloride (to the point of precipitation), and then treated with excess of quinine (and other alkaloid) acidulate solution, and filtered, when the filtrate would not precipitate mercuric chloride, on its addition in any proportions.

Regarding the iodomercurate precipitation of atropine, Mayer states* that the precipitate is $(C_{17}H_{23}NO_3HI)_2HgI_2$, "one-half the mercury of the test-liquor remaining in solution." He also makes the same remark again, thus,† "The compounds formed are hydriodates of the base with iodide of mercury; in consequence of which [?] a part of the mercury used for precipitation remains in solution." How it could be true that any part of the mercury used for precipitation remains in solution I am unable to understand, and qualitative tests indicate that it is not true. When Mayer's solution is added to alkaloid acidulate solution, not quite to complete precipitation of the alkaloid, and filtered, the filtrate yields no mercury beyond that trace due to the water solubility of the precipitate itself. Charging the filtrate with hydrogen sulphide, the solution is but slightly darkened, with no precipitate, and the same slight darkening is obtained with hydrogen sulphide in the final water washings of the precipitate. (The mercury of Mayer's solution is changed to precipitate of mercuric sulphide by action of hydrogen sulphide, and so is that of the alkaloid iodomercurate precipitates.) This evidence that no part of the mercury of the reaction is left in solution was obtained with quinine, morphine, aconitine and atropine; and obtained, alike, with Mayer's solution as it is, and with Mayer's solution which had been saturated with mercuric chloride.

It certainly appears, then, that all the mercury of a potassium iodide solution, as well as all the iodide essential to the solubility of the same, enter into the precipitates with the alkaloids,—save only such traces as correspond to the solubility of these precipitates. In accord with this conclusion, regarding the iodide, the equation for strychnine precipitation was proposed with $KIHgI_2+3KI$, instead of $(KI)_2HgI_2+2KI$, for Mayer's solution. Now, regarding the mercury—the element never in excess in our reagent—it has to be admitted, when we disprove Mayer's inexplicable statement for the atropine precipitation, that "one-half the mercury of the

* Chem. News, 7, 161. † Ibid. 159.

test-liquor remains in solution," we return to an apparent dilemma —a contradiction as to the ratio between atropine and mercury, as follows:

$C_{17}H_{23}NO_3$ to Hg, from *volumetric* indications: Mayer, 0.0145; Dragendorff, 0.0125; Günther, 0.0193; the ratio varied by conditions; the precipitate somewhat soluble.

$2C_{17}H_{23}NO_3$ to Hg, from *gravimetric* indications: Dragendorff, 0.0375 alkaloid giving 0.0379; 0.0375 giving 0.0386; 0.0420 giving 0.0409, etc., quite uniform. (Precipitate : alkaloid : : 100 : 44.9.)

The above atomic ratio for volumetric use is that of 0.0145 atropine to each cc. of the standard solution: $\frac{1}{20\,000}$ of $C_{17}H_{23}NO_3$ (289) to $\frac{1}{20\,000}$ of HgI_2+4KI ($HgCl_2$ 271 and KI 996.6). Mayer gave this, theoretical, as the working factor.* Dragendorff reports† a large number of results, pretty uniform for 0.0125 atropine to each cc of alkaloid, when the conditions were kept as follows: The dilution 350 to 500 parts for one of alkaloid; the Mayer's solution diluted with an equal bulk of water; the addition so slow that the precipitate may crystallize; the end of the reaction found by filtering a few drops and adding thereto a drop of the standard solution, and a correction made by adding 0.00005 gram alkaloid for each cc. of total solution. Günther, using a method of Dragendorff's, reports‡ 0.0193 to the cc.

For the atomic ratio found in gravimetric analysis of the atropine precipitate, having only half as much mercury to alkaloid as Mayer's volumetric ratio, I can only cite the experiments of Dragendorff,§ but they seem to be sufficient. The atropine, in acidulate solution of 350 to 400 parts, is precipitated by a slight excess of Mayer's solution, the precipitate left twenty-four hours to subside, well washed, dissolved in alcohol, and this evaporated to dryness at 100° C. Eight trials are reported, with results ranging as quoted above. Mayer gives no data for the formula he states, $(C_{17}H_{23}NO_3HI)_2HgI_2$. The discrepancy, then, is to be acknowledged as an admonition to return to further investigation. The

* Ibid. 159, 160.

† Werthbestimmung, Seite 20. Also, in part, Dragendorff and Koppe: Zeitsch. an. Chemie, 6, 309 (1867).

‡ Zeitsch. f. an. Chemie, 8, 476 (1869).

§ Werthbestimmung, S. 24. Another report may be mentioned: one made by the present writer, in 1876, from the work of Mr. J. R. Little (Am. Jour. Phar. 48, 388; Jahresbericht der Pharmacie, 1876, 525). As the absolute purity of the alkaloid taken was not made certain, the object being that of approximate assay, I could not quote the results as important in this inquiry. In triplicate trial, 0.100 of atropine gave 0.170 of precipitate. The precipitate was simply water-washed and dried.

molecular formula of atropine obtains support from the late synthetic advances of Ladenberg;* but it is an alkaloid liable to decomposition, and consequent impurity, whereby our perplexity may have arisen. Also, the composition of the iodomercurate may change in being washed with water.

In the precipitation of morphine as iodomercurate, it is well established that, when the dilution is 200 parts of acidulate solution for one part of alkaloid, each cc. of Mayer's solution precipitates very nearly 0.020 of morphine crystallized, or 0.019 of morphine anhydrous. The alkaloidal crystals, $C_{17}H_{19}NO_3H_2O=303$, are constant on the water-bath, becoming anhydrous, $C_{17}H_{19}NO_3=285$, at 120° C. The factor, 0.020 to the cc., was given by Mayer, and is sustained by Kubly and Dragendorff, who make the proviso that the dilution should be 200 to 1.†

In trials that I have made with crystallized morphine, I have found the ratio of 0.020 to one cc. to give results coming near to the quantity taken, but apt to fall a little below.‡ The solubility of the precipitate must not be disregarded: in dilutions of 1 to 4000 the reaction does not appear. In the ratio of 0.0202 gram crystallized morphine to the cc., we have $\frac{202}{10000}$ of $2C_{17}H_{19}NO_3H_2O$ for $\frac{200}{10000}$ of (HgI_2+4KI) in Mayer's solution; or 4 molecules of alkaloid for 3 atoms of mercury, indicating for the precipitate,

$$(C_{17}H_{19}NO_3)_4(HI)_2(HgI_2)_3.$$

The following analyses of the precipitate were made by Messrs. Judson & Payne, following the method previously reported—the same used for strychnine:

	Calculated from $(C_{17}H_{19}NO_3)_4(HI)_4(HgI_2)_3$		Judson and Payne.				Calculated from $(C_{17}H_{19}NO_3)_4(HI)_6(HgI_2)_3$	
			1st.	2d.	3d.	Mean.		
Iodine	1270	42.13	42.6	43.0	41.7	42.43	1524	46.61
Mercury	600	19.92	17.5	18.0	19.7	18.40	600	18.35
H of HI	4	0.13	...	...	...	0.13	6	0.18
Morph'e	1140	37.82	...	...	...	39.04	1140	34.86
	3014	100.00				100.00	3270	100.00

* Deut. Chem. Ges. Ber. 12, 941, 944.

† Werthbestimmung starkwirkender Droguen, S. 86. Zeitsch. an. Chemie, 6, 321. Results as follows:

1st, 0.0224 cryst.	morphine	to the cc.	in feebly	acid sol.	
2d, 0.0221	"	"	"	in strongly	" "
3d, 0.0191 anhyd.	"	"	"	in feebly	" "
4th, 0.0205	"	"	"	in strongly	" "

‡ The writer's report on Morphiometric Processes for Opium: Pro. Am. Phar. Asso. (1878), 26, 812; Jour. Chem. Soc. (1880), Abstracts, 192.

Groves (*loc. cit.*) obtained a mean of 42.27 per cent. iodine, and 22.74 per cent. mercury, leaving 32.91 per cent. morphine. His proposed formula was $C_{17}H_{19}NO_3HgI_2$.

In comparison, it may be noted that morphine forms $(C_{17}H_{19}NO_3)_2(HCl)_2PtCl_4$, $(C_{17}H_{19}NO_3)(HCl)(HgCl_2)_2$, and $(C_{17}H_{19}NO_3)_4I_6$.

For morphine, then, gravimetric and volumetric experiments, with the test for iodine in the filtrate, admit the following equation:

$$2(C_{17}H_{19}NO_3)_2H_2SO_4+(KI)_4(HgI_2)_3+8KI=$$
$$(C_{17}H_{19}NO_3HI)_4(HgI_2)_3+8KI+2K_2SO_4.$$

In the quinine precipitation, it is stated that one cc. of Mayer's solution precipitates 0.0108 gram of anhydrous alkaloid. I am unable to cite any volumetric determinations in support of this ratio. The anhydrous alkaloid is obtained at 125° C. The crystallization water of the sulphate is not uniform. The factor 0.0108 is $\frac{2}{300}$ of two-thirds the molecular weight, 324, and indicates the molecule of the precipitate to be $(C_{20}H_{24}N_2O_2)_2(HI)_x(HgI_2)_3$. The percentages obtained by Messrs. Judson and Payne do not accord with this formula, whether we take two, three, or four of (HI). The following is a comparison of one of these formulae:

	Calculated from $(C_{20}H_{24}N_2O_2)_2(HI)_3(HgI_2)_3$		Judson and Payne. 1st.	2d.	3d.	Mean.
Iodine	1143	47.74	47.10	48.30	47.80	47.73
Mercury	600	25.06	20.90	20.10	19.60	20.20
H of HI	3	0.13	...	...	...	0.13
Quinine	648	27.07	...	...	...	31.94
	2394	100.00				100.00

Some time since, a determination of the weight of iodomercurate precipitate of quinine, made by Messrs. Johnston and Lobb, was reported by the writer.* The quinine taken was dried, from the trihydrate, at 100° C. The precipitate was washed, and dried at 100° C. There were obtained,

1st,	from	0.280	of quinine,	0.801	of iodomercurate.
2d,	"	0.280	" "	0.824	" "
3d,	"	0.280	" "	0.812	" "
Mean,	"	1.000	" "	2.900	" "

*Am. Jour. Phar. 49, 482 (Oct. 1877); Jahresbericht der Pharmacie, 1877, 419; Phar. Jour. Trans. [3], 8, 407.

If we accept the proportion of 4.28 per cent. of water retained in quinine hydrate dried on the water-bath (Allen, referred to, *Ibid.*), we have 2.485 of precipitate from 1.000 of anhydrous quinine; or 33.01 per cent. of alkaloid in the precipitate, against the 31.94 per cent. of Judson and Payne. Groves* obtained a mean of 23.25 per cent. of mercury; and 46.60 per cent. of iodine, in the precipitate.

From the berberine precipitate, Messrs. Judson and Payne obtained a mean of 4.17 per cent. (40.8, 41.0, 37.7) of iodine; and a mean of 7.73 (7.5, 7.7, 8.0) per cent. of mercury; leaving a mean of 52.10 per cent. of alkaloid. In 1876 I reported† some results of work by Mr. Beach, giving very nearly 2 parts iodomercurate from one part of berberine. Excess of the standard solution did not vary the weight of the precipitate.

Certainly it is desirable to have analyses of these precipitates with direct estimations of the alkaloids in them. Otherwise, the question of hydration is unsettled. The quantity of precipitate made from a solution of a unit of alkaloid becomes an uncertain datum, in most cases, owing to a degree of solubility of the precipitate.

Some determinations of *the proportions of iodide and mercuric salt* needful for solutions were made by Mr. HUGO LUPINSKI,‡ and should be here reported. Four twentieth-normal solutions were made, as follows:

No. 1. Mercuric chloride, 13.55; potassium iodide, 33.22; water to one litre. $HgCl_2 + 4KI = HgI_2 + 2KI + 2KCl$. Some red mercuric iodide remained undissolved. This dissolved when heated, and crystallized on cooling.

No. 2. Mercuric chloride, 13.55; potassium iodide, 33.22; potassium bromide, 2.9825; water to one litre.

$$HgCl_2 + 4KI + \tfrac{1}{2}KBr = HgI_2 + 2KI + \tfrac{1}{2}KBr + 2KCl.$$

Complete solution required heat, and on cooling there was a crystalline deposit of red iodide of mercury.

No. 3. Mercuric chloride, 13.55; potassium iodide, 33.22; potassium bromide, 5.965; water to one litre.

$$HgCl_2 + 4KI + KBr = HgI_2 + 2KI + KBr + 2KCl.$$

Dissolved readily and did not deposit on standing four weeks.

Solution No. 3 was used, with the idea that it furnished potas-

* Jour. Chem. Soc. 11, 101.

†Am. Jour. Phar. 48, 385; Jahresbericht der Phar. 1876, 524.

‡ Graduation Thesis, Univ. Mich. 1878.

sium mercuric iodide of the more stable composition of $(KI)_2 HgI_2$, with no excess of iodide, and in a permanent solution. It was thought that, with most alkaloids, the bromide would not react at all.

Using this solution, No. 3, Mr. Lupinski made a diligent search for *an indicator of the end of the reaction*, with alkaloids. (1) A paper wet with saturated mercuric chloride and dried was used—to reveal the presence of an excess of the standard solution, in estimation of alkaloids. The indicator worked well, except that it was not delicate enough. (2) A solution of potassium and ammonium hydrates; to give the mercurammonium iodide, when excess of the reagent was attained, with alkaloid acidulous solutions. The alkali hydrates react with the alkaloid precipitates, and therefore do not serve. (3) A solution of iodic acid and starch, to show when excess of soluble iodide had been attained. This, too, reacted with the precipitates, and was inoperative.

A proposition was made by Mr. Mayer* to find the end of the reaction, by adding excess of the Mayer's solution, and then "without filtering" titrating back with tenth-normal solution of silver nitrate, using normal chromate of potassium as an indicator, in the common way. Each cc. of the standard potassium mercuric iodide to require 4 cc. of the corresponding silver solution. Mr. Lupinski† calls attention to the essential defect in this plan, that it disregards the accumulation of the potassium chloride of Mayer's solution during the precipitation of alkaloids. Also, the excess of potassium iodide would interfere in the same way. The erroneous results of titrating back with Mayer's solution may be placed before the eye by an equation for the morphine precipitation (given before without statement of the chloride present):

$$2(C_{17}H_{19}NO_3)_2H_2SO_4+3(HgI_2+4KI+2KCl)=$$
$$(C_{17}H_{19}NO_3HI)_4(HgI_2)_3+8KI+6KCl+2K_2SO_4.$$

With no excess of the Mayer's solution, there are still 8KI+6KCl to titrate back with the silver solution. Mr. Mayer offers this use of the silver solution, "where no coloring matters, or substances affecting nitrate of silver are present." On trial, some time ago, I found that some of the alkaloid iodomercurate precipitates gradually decompose silver nitrate, in solution, by contact at common temperatures.

*Chem. News, 7, 159, April 4, 1863.

† Thesis, before cited.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ETHERS OF URIC ACID.*

VI.—DIMETHYLURIC ACID.

BY H. B. HILL AND C. F. MABERY.

Dimethyluric acid is formed when diplumbic urate is heated with methyl iodide according to the general method which one of us has already described† for making the monomethyl compound. The preparation of considerable quantities of pure substance by this method is, however, a matter of some difficulty, and we have found that a close attention to details is necessary to insure success.

The diplumbic urate which we used at first was made according to the directions of Allan and Bensch,‡ by precipitating a boiling solution of plumbic nitrate with dipotassic urate purified by alcohol. Although we heated this lead salt with an excess of methyl iodide at various temperatures (100° to 170°) for different lengths of time (five to ninety hours), we could not succeed in obtaining from it a product which did not contain quite a large percentage of the monomethyl ether. We therefore attempted to effect the separation of the monomethyl and dimethyl compounds by fractional crystallization, or by methods based upon differences in the behavior of their salts; but we were unable to find a method which was at all satisfactory, and, after many experiments, convinced ourselves that it was necessary to obtain from the first a product essentially free from the monomethyl compound.

After a long series of experiments which need not be described in detail, we found that such a product could be obtained from a lead salt made by precipitating with the diplumbic urate a small amount of plumbic hydrate. We have made no experiments to show how small this quantity of plumbic hydrate can be made with safety, as it seemed a matter of little importance. In preparing the lead salt we dissolved uric acid in a potassic hydrate solution of

* Communicated by the Authors. Proceedings Amer. Acad. Arts and Sciences.

† Proceedings Amer. Acad. Arts and Sciences, 12, 27.

‡ Ann. Chem. u. Pharm. 65, 191.

known strength, using twenty per cent. more potassic hydrate than was theoretically required to form the dipotassic urate, and poured this alkaline solution into a boiling dilute solution of plumbic nitrate. After washing the bulky precipitate with hot water we usually washed with alcohol, and finally with a little ether; partly to facilitate the drying, and partly because the lead salt was in this way obtained in a much more compact and convenient form. After drying at 100° the salt was well powdered and dried at 160°.

In order to insure complete decomposition of the lead salt, which evidently is essential to prevent the formation of monomethyluric acid, we have found it necessary to take a slight excess of methyl iodide, to dilute it with an equal weight of ether, and, after mixing thoroughly with the lead salt, to heat for twenty hours at 165°. We have also found it advantageous to allow the tube to cool after heating for twelve to fifteen hours, and to mix the contents thoroughly by shaking before heating further.

After distilling off the ether and the slight excess of methyl iodide, the solid product of the reaction is extracted with boiling water, and the lead precipitated by hydric sulphide. The solution filtered boiling hot deposits on cooling crystals of dimethyluric acid which may be purified by recrystallization from hot water. In this way we have obtained about fifty per cent. of the theoretical yield of well crystallized product apparently pure. Since monomethyl and dimethyluric acids differ in the amount of carbon they contain only by 3.29 per cent., it is evident that the absolute purity of our product could not be determined by analysis.

Dimethyluric acid crystallizes usually in slender oblique prisms, often concentrically grouped, which contain a molecule of crystal water. From saturated solutions where crystallization takes place at a high temperature we have not unfrequently obtained small, compact, pointed prisms, which contain less water and very possibly are anhydrous. The behavior of both of these forms to polarized light shows that they belong to one of the oblique systems. The acid begins to turn brown when heated to about 340°; at higher temperatures it melts, with decomposition and partial sublimation. It is quite soluble in boiling water, sparingly soluble in cold water, still less so in alcohol, and insoluble in ether. Concentrated sulphuric and hydrochloric acids dissolve it readily, and deposit the greater portion upon dilution.

The slender oblique prisms in which methyluric acid ordinarily

crystallizes contain one molecule of water when dried *in vacuo* over sulphuric acid.

0.6067 gram lost at 160° 0.0511 gram H_2O=8.49 per cent.

The formula $C_5H_2(CH_3)_2N_4O_3 . H_2O$ requires 8.41 per cent.

The crystals of the second form were obtained for analysis by evaporating a saturated solution of the acid upon the water-bath, and filtering hot. Although our determinations agree closely with the amount required for a half-molecule of water, it is not impossible that the loss in weight is due to hygroscopic moisture, as was the case with the monomethyl acid.

I. 0.4547 gram substance dried *in vacuo* lost at 160° 0.0196 gram H_2O=4.31 per cent.

II. 0.2651 gram lost 0.0114 gram H_2O=4.30 per cent.

The formula $C_5H_2(CH_3)_2N_4O_3 . \frac{1}{2}H_2O$ requires 4.39 per cent.

The composition of the substance dried at 160° was determined by the following analyses:

I. 0.2747 gram gave 0.1097 gram H_2O and 0.4291 gram CO_2.

II. 0.2022 gram gave 0.0789 gram H_2O and 0.3167 gram CO_2.

III. 0.1393 gram gave 0.0557 gram H_2O and 0.2185 gram CO_2.

IV. 0.3521 gram gave 86 cc. nitrogen at 16° and 756.5 mm. pressure.

	Calculated for $C_5H_2(CH_3)_2N_4O_3$	Found. 1.	2.	3.	4.
C	42.85	42.60	42.72	42.78	...
H	4.08	4.44	4.34	4.44	
N	28.57	...	...	...	28.21

The solubility in boiling water was determined by filtering a boiling saturated solution through a hot-water filter into weighed flasks. After cooling, the flasks were weighed, the contents transferred to platinum dishes, evaporated to dryness, and the residue dried at 165°.

I. 54.2110 grams solution left 0.2043 gram residue.

II. 57.8596 grams solution left 0.2940 gram residue.

The boiling saturated solution contains the following percentages:

1.	2.
0.5152	0.5081

To determine the solubility in cold water a hot solution was kept at 20° for four hours with occasional stirring. The solution was then filtered into weighed platinum crucibles, evaporated to dryness, and the residue heated at 160°.

I. 35.6147 grams solution left 0.0189 gram residue.
II. 25.2221 grams solution left 0.0134 gram residue.
III. 21.9260 grams solution left 0.0116 gram residue.
The solution saturated at 20° contained in percentages:

1.	2.	3.
0.0531	0.0532	0.0529

Taking the mean of these results, dimethyluric acid requires for solution 195.2 parts boiling water and 1885.3 parts of water at 20°.

An aqueous solution has a slight acid reaction, and decomposes carbonates on heating. A solution in sodic or potassic hydrate is not precipitated by carbonic dioxide. From concentrated cold solutions it is precipitated by stronger acids in a gelatinous form; from more dilute solutions it separates in crystals.

Salts of Dimethyluric Acid.

Dipotassic dimethylurate.

$K_2C_5(CH_3)_2N_4O_3 . 4H_2O$.

Dimethyluric acid was dissolved in an excess of a dilute solution of potassic hydrate, the clear solution boiled for several minutes, and about ten volumes of alcohol added. The crystalline precipitate, which separated on standing, was filtered off rapidly by the pump, washed with alcohol, and dried *in vacuo* over sulphuric acid and potassic hydrate. This salt crystallizes in fine silky needles, which are very soluble in water. It absorbs carbonic dioxide very rapidly from the air, probably forming the monopotassic salt.

To determine the water of crystallization the salt was heated in a current of dry air, free from carbonic dioxide.

0.8079 gram salt dried *in vacuo* gave 0.1662 gram H_2O=20.57 per cent. Calculated for $K_2C_5(CH_3)_2N_4O_3 . 4H_2O$ 20.92 per cent.

0.3198 gram anhydrous salt gave 0.1766 gram KCl. K=28.95 per cent. Calculated for $K_2C_5(CH_3)_2N_4O_3$ 28.73 per cent.

Monopotassic dimethylurate.

$KC_5H(CH_3)_2N_4O_3 . 1\frac{1}{2}H_2O$.

Potassic carbonate, in slight excess of the theoretical amount, is added to the acid suspended in boiling water. The solution is boiled for some time, and the salt precipitated by adding about ten

volumes of alcohol. It is then filtered, washed with alcohol, and dried *in vacuo* over sulphuric acid. The salt crystallizes in branching needles, which are quite soluble in water.

0.2540 gram salt dried *in vacuo* gave 0.0278 gram H_2O=10.94 per cent. Calculated for $KC_5H(CH_3)_2N_4O_3 . 1\frac{1}{2}H_2O$ 10.35 per cent.

0.2180 gram anhydrous salt gave 0.0702 gram KCl. K=16.88 per cent. Calculated for $KC_5H(CH_3)_2N_4O_3$ 16.70 per cent.

Disodic dimethylurate.

$Na_2C_5(CH_3)_2N_4O_3 . 4\frac{1}{2}H_2O.$

This salt is precipitated from a sodic hydrate solution of the acid by alcohol in the same way as the dipotassic salt. It crystallizes in needles much larger than those of the corresponding potassic salt.

0.3064 gram salt dried *in vacuo* gave 0.0780 gram H_2O=25.46 per cent. Calculated for $Na_2C_5(CH_3)_2N_4O_3 . 4\frac{1}{2}H_2O$ 25.23 per cent.

0.2234 gram anhydrous salt gave 0.1074 gram NaCl. Na=18.91 per cent. Calculated for $Na_2C_5(CH_3)_2N_4O_3$ 19.17 per cent.

Monosodic dimethylurate.

$NaC_5H(CH_3)_2K_4O_3 . 2H_2O.$

This salt was made in the same way as the monopotassic salt. It forms microscopic needles which are more soluble in water than the potassic salt.

0.5327 gram salt dried *in vacuo* gave 0.0798 gram H_2O=14.98 per cent. Calculated for $NaC_5H(CH_3)_2N_4O_3 . 2H_2O$ 14.18 per cent.

0.3069 gram anhydrous salt gave 0.0638 gram NaCl. Na=10.17 per cent. Calculated for $NaC_5H(CH_3)_2N_4O_3$ 10.54 per cent.

Dibaric dimethylurate.

$BaC_5(CH_3)_2N_4O_3 . 3H_2O.$

Dimethyluric acid was dissolved in as little boiling water as possible, a solution of baric hydrate added in slight excess of the amount theoretically required, and the solution boiled. The salt separated as the solution cooled, and was purified by recrystallization from hot water. It was filtered rapidly and dried *in vacuo* over sulphuric acid and potassic hydrate. The salt is quite soluble in hot, but slightly soluble in cold water. When cooled rapidly it forms a jelly-like mass, but when cooled slowly it crystallizes in flat, transparent prisms.

0.2177 gram salt dried *in vacuo* gave 0.0307 gram H_2O=14.10 per cent. Calculated for $BaC_5(CH_3)_2N_4O_3 . 3H_2O$ 14.03 per cent.

0.1875 gram anhydrous salt gave 0.1335 gram $BaSO_4$. Ba= 41.86 per cent. Calculated for $BaC_5(CH_3)_2N_4O_3$ 41.89 per cent.

Monobaric dimethylurate.

$Ba(C_5H(CH_3)_2N_4O_3)_2 . 3H_2O.$

This salt was made by boiling an aqueous solution of the acid with baric carbonate, filtering, and precipitating the filtrate with alcohol.

0.3661 gram salt dried *in vacuo* gave 0.0342 gram H_2O=9.34 per cent. Calculated for $Ba(C_5H(CH_3)_2N_4O_3)_2 . 3H_2O$ 9.29 per cent.

0.3350 gram anhydrous salt gave 0.1491 gram $BaSO_4$. Ba= 26.17 per cent. Calculated for $Ba(C_5H(CH_3)_2N_4O_3)_2$ 25.99 per ct.

Further study of the salts of dimethyluric acid seemed to us of no immediate importance, since the results we had reached served to establish beyond all doubt its dibasic character.

Action of Hydrochloric Acid.

Dimethyluric acid, when heated with concentrated hydrochloric acid, is completely decomposed, giving products perfectly analogous to those described by Strecker* as resulting from the decomposition of uric acid, and qualitatively identical with those obtained under the same conditions from methyluric acid.

The dimethyluric acid was heated for several hours with hydrochloric acid saturated at 0° to 170°. The liquid from the tubes, which showed great pressure on opening, was evaporated to dryness on the water-bath, the residue dissolved in water and distilled with plumbic hydrate in a current of steam as long as the distillate gave an alkaline reaction. The distillate was caught in hydrochloric acid, evaporated to dryness on the water-bath, and the residue treated with a mixture of absolute alcohol and ether. Ammonic chloride was left undissolved, while in solution was a salt which gave qualitative tests characteristic of the monamines. The platinum salt, recrystallized from water, gave on analysis:

0.5421 gram left on ignition 0.2261 gram platinum.

	Calculated for $(CH_3NH_2)_2PtCl_4$.	Found.
Pt	41.61	41.75

* Ann. Chem. u. Pharm. 146, 142; Zeitschr. für Chemie, 1868, 215.

In order to find the relative amounts of ammonia and methylamine which were formed in this reaction, we determined the percentage of chlorine in the saline residue as obtained by distillation with plumbic hydrate. The residue of chlorides was dried at 100° and the chlorine precipitated by argentic nitrate.

0.6365 gram mixed chlorides gave 1.4681 gram $AgCl \cdot Cl_2$ = 57.07 per cent. Calculated for 2 molecules methylamine chloride and 1 molecule ammonic chloride = 56.50 per cent.

Two molecules of methylamine are therefore formed in the reaction and one molecule of ammonia.

The liquid remaining in the flask, after the distillation, was filtered hot, the lead precipitated as sulphide, and the filtered solution concentrated. On long standing crystals of glycocol separated, which, for identification, were converted into the copper salt by boiling with freshly precipitated cupric oxide, and precipitating the filtered solution with alcohol.

0.4757 gram copper salt lost at 135° 0.0391 gram H_2O.

	Calculated for $(C_2H_4NO_2)_2Cu \cdot H_2O$.	Found.
H_2O	7.85	8.22

0.4291 gram anhydrous salt left on ignition 0.1611 gram CuO.

	Calculated for $(C_2H_4NO_2)_2Cu$.	Found.
CuO	37.55	37.54

The reaction may therefore be written:

$$C_5H_2(CH_3)_2N_4O_3 + 5H_2O = 3CO_2 + NH_3 + 2CH_3NH_2 + C_3H_5NO_2.$$

Oxidation of Methyluric Acid.

By the oxidation of dimethyluric acid with nitric acid we were unable to obtain a crystalline product. Since the crystalline amalic acid would undoubtedly have been formed had the two methyl radicals been attached to the same urea residue, we concluded that our syrupy oxidation product contained methylalloxan, and for its identification converted it at once into the calcic methylalloxanate. We followed closely the method which one of us had already described,* and found to give constant results. Dimethyluric acid was dissolved in the smallest possible quantity of nitric acid of sp. gr. 1.42, the solution diluted with water, and the excess of acid

* Proceedings Amer. Acad. Arts and Sciences, 12, 33.

neutralized with calcic carbonate in the cold. After the solution was freed as nearly as possible from carbonic dioxide, by allowing it to stand for some time *in vacuo*, it was largely diluted with alcohol, filtered, and the calcic methylalloxanate precipitated by the cautious addition of ammonia. The carbon and hydrogen were estimated in this salt dried at 100° by a combustion in a stream of oxygen, the calcium by ignition with sulphuric acid.

I. 0.2334 gram substance gave 0.2103 gram CO_2, 0.0439 gram H_2O, and 0.0921 gram residue. This residue gave 0.1489 gram $CaSO_4$, equivalent to 0.0611 gram calcic oxide. The residue, therefore, contained 0.0311 gram CO_2.

II. 0.2172 gram gave 0.1401 gram $CaSO_4$.

III. 0.2268 gram gave 0.1448 gram $CaSO_4$.

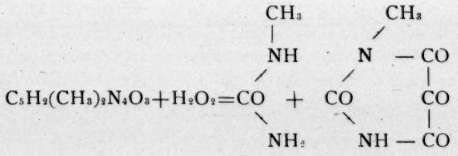
	Calculated for $C_4H(CH_3)_3N_2O_3Ca$.	Found. 1.	2.	3.
C	28.30	28.20		
H	1.88	2.09		
Ca	18.87	18.77	18.97	18.78

In confirmation of these results it seemed advisable to isolate the methylurea which should be formed as the second product of the reaction. We therefore oxidized with hydrochloric acid and potassic chlorate, according to the method of Schlieper, evaporated at a gentle heat until the greater part of the excess of hydrochloric acid was driven off, and then separated from the potassic chloride with absolute alcohol. The residue left by the evaporation of the alcohol at a low temperature gave with nitric acid crystals of methylurea nitrate, which were purified by pressing between folds of paper and recrystallization from water.

0.2464 gram gave 0.1635 gram CO_2 and 0.1147 gram H_2O.

	Calculated for $C_2H_7N_3O_4$.	Found.
C	17.81	18.09
H	5.11	5.15

This reaction may therefore be written:



By the oxidation with potassic chlorate we have, however, invariably observed the formation of a small quantity of a crystalline substance, which we have as yet been unable to obtain in sufficient quantity for investigation. When the residue obtained by evaporation after oxidation was diluted with water, well-formed transparent prisms, pointed at either end, gradually separated, which could be recrystallized from hot water. The quantity formed was extremely small, and, although we modified the process in many ways, we have thus far been unable to increase the yield. At present, therefore, we can do no more than describe the few experiments we have been able to make with the small quantity at our disposal. The substance was readily soluble in hot water, sparingly soluble in cold water or in alcohol. In concentrated nitric acid it dissolved on warming, and crystallized out apparently unchanged on cooling. With ammonia it gave no red color. On heating it melted at about 160°. An analysis gave numbers which correspond more nearly with those required by $C_5H_6N_2O_3$ than by any other simple formula.

0.2078 gram gave 0.3259 gram CO_2 and 0.0788 gram H_2O.

0.1459 gram gave 25.6 cc. nitrogen at 16° and 720 mm. pressure.

	Calculated for $C_5H_6N_2O_3$.	Found.
C	42.26	42.77
H	4.23	4.21
N	19.72	19.27

Although the substance possessed acid properties, we were unable to prepare its salts. On boiling with a solution of baric hydrate it was decomposed with the separation of baric carbonate. In the distillate the presence of ammonia and an amine, without doubt methylamine, could be proved by qualitative tests, and in the residue was an acid whose barium and lead salts were sparingly soluble in water, but which we were unable to identify on account of our very limited supply of material.

By the long-continued action of nitric acid upon dimethyluric acid methylparaban is formed. After boiling with nitric acid of sp. gr. 1.3 till a drop of the solution gave no coloration with ammonia, the solution was evaporated on the water-bath until the excess of acid was driven off and the syrupy residue diluted with a little water. The crystals which separated were pressed with paper and recrystallized from hot water.

Thus prepared the substance melted at 149°, sublimed slowly at 100°, readily at higher temperatures, and gave on analysis the percentages corresponding to methylparaban.

0.2838 gram gave 0.3886 gram CO_2 and 0.0879 gram H_2O.

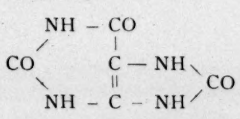
	Calculated for $C_2H(CH_3)N_2O_3$.	Found.
C	37.50	37.35
H	3.13	3.45

By the oxidation of dimethyluric acid with potassic permanganate in alkaline solution, we have been unable to prepare the corresponding dimethylallantoin. The acid either undergoes a more radical decomposition, or more probably the assimilation of water takes place more readily than in case of allantoin or even methylallantoin and the dimethylallantoic acid results.

We made several attempts to isolate from the uncrystallizable product of the oxidation various salts of the dimethylallantoic acid, but found them so uninviting in their character that we could hardly hope to effect their purification.

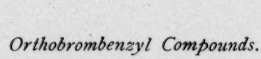
Since considerable time must of necessity elapse before further results can be obtained in this investigation, it may not be out of place to call attention to one inference concerning the structure of uric acid which may fairly be drawn from the facts thus far established.

It has been shown that the two hydrogen atoms of uric acid which are replaced in the formation of salts are directly connected with two different nitrogen atoms; furthermore, when methyl groups are introduced in the place of these hydrogen atoms, that two other hydrogen atoms may then be replaced by metals. The only simple explanation of this behavior would seem to be that the four hydrogen atoms of uric acid are attached to four different nitrogen atoms, and that only two of these hydrogen atoms can be replaced at the same time by strongly basic radicals. Of the many structure-formulae which have thus far been proposed for uric acid, only two contain this arrangement of the hydrogen atoms. These are the formulae of Medicus,*—



* Ann. Chem. u. Phar. 175, 243.

and of Fittig,*—



Further discussion of these formulae, or of others fulfilling the same conditions, must be reserved for a subsequent paper.

VII.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

ORTHOBROMBENZYL COMPOUNDS†

By C. Loring Jackson and J. Fleming White.

The substances described in this paper are the first substituted benzyl compounds belonging to the ortho series known; unless, indeed, the orthochlorbenzaldehyde, made from salicylic aldehyde,‡ be included in this class. They were made from the orthobrombenzylbromide,§ which was described in the first paper of this series as an oily liquid that did not solidify even at —15°. The specimen on which that experiment was tried could not have been perfectly pure, as we have since found that orthobrombenzyl bromide solidifies near zero in large rhombic crystals, often one centimeter in diameter, which melt at 30¼°, and can be recrystallized from alcohol or ligroine. An analysis gave the following result:

0.3570 gr. of substance gave 0.5380 gr. AgBr.

	Calculated for $C_7H_6Br_2$.	Found.
Bromine	64.00	64.13

Orthobrombenzylalcohol, $C_6H_4BrCH_2OH$, was made by the action of aqueous ammonia at 160° in a sealed tube on the acetate obtained by boiling the bromide with an alcoholic solution of sodic acetate. As its melting-point (80°) was much higher than expected, we also prepared it by heating the acetate with alcoholic potassic hydrate in a sealed tube, and by boiling the bromide with water for two days; and found that the products of all these methods melted at

* Grundniss der organischen Chemie, 10th edition, 309.

† Presented to the American Academy. Communicated by the Authors.

‡ Henry, Ber. d. ch. G., 1869, 136.

§ This Journal, Vol. 1, 100.

the same point (80°), so there can be no doubt that this is the true melting-point of the alcohol. An analysis of the substance made by the first method gave the following results:

0.5543 gr. of substance dried *in vacuo* gave on combustion 0.9131 gr. CO_2 and 0.1990 gr. H_2O.

0.3480 gr. gave, by the method of Carius, 0.3498 AgBr.

	Calculated for C_7H_6BrOH.	Found.
Carbon	44.92	44.94
Hydrogen	3.74	3.99
Bromine	42.79	42 78

Properties. Slightly flattened, white needles, sometimes 5 cm. long, when crystallized from boiling water, from ligroine needles grouped in sheaves, with but little odor, which melt at 80°, sublime in oily drops, and distil with steam very easily. It is very slightly soluble in cold, much more so in hot water or ligroine, and freely in alcohol, ether, benzol, glacial acetic acid, and carbonic disulphide. It can be most conveniently purified by crystallization from hot ligroine. Oxidized with potassic permanganate, it gave ortho-brombenzoic acid, melting point 147°–148°.

The *Orthobrombenzylcyanide*, prepared by boiling alcoholic potassic cyanide with the bromide, a dark-colored oil, which did not solidify in a freezing mixture, and seemed to be decomposed by distillation; we therefore did not attempt to purify and analyze it

The *Orthobromalphatoluic Acid*, $C_6H_4BrCH_2COOH$, was made from the cyanide by heating it with strong hydrochloric acid to 130° in a sealed tube. The product was purified by conversion into the ammonium salt and recrystallization from water or alcohol of the acid set free from this by dilute sulphuric acid.

It forms white pearly plates, or flattened needles, melting at 102½° –103°; but little soluble in cold, more so in hot water, freely in alcohol, ether, benzol, glacial acetic acid, and carbonic disulphide. It is only sparingly soluble in cold ligroine, but very soluble in hot, from which it crystallizes in small needles arranged in fan-shaped groups.

Argentic Orthobromalphatoluate, $C_6H_4BrCH_2COOAg$, made from the acid by adding ammonic hydrate, driving off the excess of ammonia on the water-bath, and precipitating with argentic nitrate, formed a white mass made up of small needles. It was washed with water, dried *in vacuo*, and analyzed.

0.2686 gr. of the salt gave 0.1200 gr. AgCl.

	Calculated for $C_8H_6BrO_2Ag$.	Found.
Silver	33.54	33.62

It is slightly soluble in boiling water, freely in dilute nitric acid.

Calcic Orthobromalphatoluate, Ca $C_6H_4BrCH_2COO)_2$, made by boiling an aqueous solution of the acid with calcic carbonate, and evaporating the filtrate, gave, dried *in vacuo*, the following result:

0.24969 gr. of the salt gave 0.0300 gr. CaO.

	Calculated for $(C_8H_6BrO_2)_2Ca$.	Found.
Calcium	8.54	8.58

It crystallizes from a very concentrated hot solution in circular groups of radiating needles, very soluble in water, somewhat less so in alcohol.

The *barium* salt formed an amorphous mass, like varnish.

A solution of the ammonium salt gave the following precipitates: with a salt of copper, *bluish green;* with ferric chloride, *orange brown;* with mercurous or plumbic salts, *white;* all of which resembled those obtained with the parabromalphatoluic acid.

Orthobrombenzylsulphocyanate, $C_6H_4BrCH_2SCN$, is an oil which does not solidify in a freezing mixture of snow and salt. It was not analyzed.

Orthobrombenzylamines. The product of the action of alcoholic ammonia on orthobrombenzylbromide at 100°, for two hours, consisted of crystals of the tertiary amine, and a liquid containing the primary and secondary amines and ammonia, with their bromides. After filtering, the crystals were washed with cold alcohol, sodic hydrate, and finally water, and then recrystallized from warm ether till they gave a constant melting-point (121½°–122°). The filtrate from the crystals was evaporated to dryness, and treated with carbonic dioxide to convert any free primary amine into carbonate. Upon washing with water, the salts of the primary amine and ammonia dissolved, leaving the secondary amine as an oil, which, after washing with sodic hydrate, was converted into the chlorplatinate by addition of chlorplatinic acid to its alcoholic solution. To the filtrate from the secondary amine, sodic hydrate was added, and the oily primary amine thus obtained washed with water until it was free from ammonia, care being taken not to expose it to the carbonic dioxide of the air.

Monorthobrombenzylamine, $C_6H_4BrCH_2NH_2$, is a colorless oil,

insoluble in water, but soluble in ether, which absorbs carbonic dioxide from the air very readily, becoming converted into the carbonate.

The *carbonate*, made most easily by allowing an ethereal solution of the free base to evaporate in the air, forms small white crystals; melting-point 95°; and is soluble in water and alcohol.

The *chloride*, made by adding hydrochloric acid to the carbonate, crystallizes in white radiating needles, or from alcohol in small curled needles; melting-point, 208°; and is soluble in water and alcohol.

The *chlorplatinate*, $(C_6H_4BrCH_2NH_3)_2PtCl_6$, is precipitated on adding chlorplatinic acid to the free base; an analysis gave 0.1990 gr. of substance gave 0.0505 gr. Pt.

	Calculated for $(C_7H_6BrNH_3)_2PtCl_6$.	Found.
Platinum	25.16	25.38

It forms indistinct orange-yellow needles, sparingly soluble in water, decidedly so in alcohol, and insoluble in ether.

Diorthobrombenzylamine was made by treating the chlorplatinate with sulphuretted hydrogen, washing the chloride out of the platinic sulphide with hot alcohol, and precipitating the free base with sodic hydrate from the solid chloride. In this way an oil was obtained, which solidified after some time in well-marked rhombic crystals, with an agreeable smell, melting at 36°, and soluble in all the ordinary solvents, with the exception of water.

Diorthobrombenzylamine Chlorplatinate, $[(C_6H_4BrCH_2)_2NH_2]_2PtCl_6$, prepared as already described, was purified by washing with alcohol and water, dried at 70°, and analyzed.

0.5840 gr. of the salt gave 0.1030 gr. Pt.

	Calculated for $[(C_7H_6Br)_2NH_2]_2PtCl_6$.	Found.
Platinum	17.58	17.66

A yellow obscurely crystalline precipitate, slightly soluble in water and alcohol, insoluble in ether.

The *chloride*, made by adding hydrochloric acid to an alcoholic solution of the free base, separates out as the alcohol evaporates, in groups made up of a few radiating white needles, which melt at 166°, are but slightly soluble in cold water, more soluble in hot and in alcohol, sparingly in ether.

Triorthobrombenzylamine, $(C_6H_4BrCH_2)_3N$, gave the following result on analysis:—

0.3245 gr. of substance gave 0.3488 gr. AgBr.

	Calculated for $(C_7H_6Br)_3N$.	Found.
Bromine	45.80	45.73

It forms small prisms with an adamantine lustre, melting at 121½°–122° and subliming in oily drops; almost insoluble in H_2O and alcohol; slightly soluble in cold, freely in hot ligroine, and in ether and benzol.

Triorthobrombenzylamine Chlorplatinate, $[(C_6H_4BrCH_2)_3NH]_2PtCl_6$, made by adding chlorplatinic acid to an ethereal solution of the amine, gave the following result on analysis:

0.3971 gr. of the salt gave 0.0540 gr. Pt.

	Calculated for $[(C_7H_6Br)_3NH]_2PtCl_6$.	Found.
Platinum	13.51	13.60

A whitish yellow, barely crystalline precipitate, insoluble in water and ether, and very slightly, if at all, soluble in alcohol.

On boiling the tertiary amine with dilute alcohol and hydrochloric acid, it dissolved, and on cooling deposited white spheres made up of radiated needles; but an analysis of the substance gave an amount of chlorine too low for the pure chloride, and we did not think the compound of sufficient importance to study it further.

LABORATORY NOTES FROM THE UNIVERSITY OF CINCINNATI.

XV.—THE CONSTITUTION OF THE TARTRATES OF ANTIMONY.

By F. W. Clarke and Helena Stallo.

For many years the so-called tartrates of antimony have been universally regarded as salts in which a peculiar univalent group, SbO, is present as a base. The fact that all of them contain oxygen in excess of that appertaining to the tartaric acid, usually in the ratio of one atom to every atom of antimony, has been the main justification of this view—a view which hitherto has seemed to be almost a necessity. In the following pages we shall endeavor

to show that, as far as these compounds are concerned, the hypothesis of any such radicle is wholly superfluous; that all or nearly all of them may be more intelligibly interpreted upon the supposition that they are derived directly from trivalent antimony, and that some of them represent a new acid, of which the above-named metal is a constituent.

The experimental part of our investigation is based upon a fact which has long been known, namely, that when tartar emetic is added to solutions of certain metallic salts, double decomposition ensues and new compounds are precipitated, in which the other metals replace the potassium of the original double tartrate. For example, tartar emetic gives with barium chloride a double salt which is ordinarily represented by the formula $C_8H_8Ba(SbO)_2O_{12}$. $2H_2O$. That is, the univalent potassium has exchanged places with the bivalent barium, the tartaric nucleus and the antimony having been transferred together as though they formed a single acid group. The preparation of the complex acid representing this group was the first object of our researches.

A quantity of the barium salt corresponding to tartar emetic having been carefully prepared, it was suspended in water and decomposed by an exactly equivalent amount of dilute sulphuric acid. Barium sulphate was of course thrown down, and, upon filtering, a strongly acid solution was obtained, rich in antimony. At first the filtrate was turbid, a fact which we erroneously attributed to the transmission of finely divided barium sulphate through the filter. We soon found, however, that even the refiltered solution, though perfectly clear at first, soon became milky, and that a sediment was deposited containing antimony. We had then a solution of an antimony compound, though plainly one of decided instability. It proved to be the sought-for acid of which tartar emetic is the potassium salt.

The properties of this acid are in certain respects very remarkable. We have already stated that upon standing it deposits a white precipitate, evidently in consequence of decomposition. The rate of deposition depends upon temperature and the degree of dilution, taking place most rapidly with warmth, and in concentrated solutions. An excess of sulphuric acid instantly brings it about, a point which must be carefully regarded in the preparation of the compound. Upon heating the acid a series of changes occur which we believe to be unique in their character. Below 30°

the solution remains tolerably clear, and the precipitate forms but slowly. At temperatures only a degree or two higher it is deposited most copiously, and assumes a curdy appearance. If now the liquid with the precipitate in it be evaporated to dryness over a water-bath, the white curds gradually disappear, and at last a transparent gummy mass is left. This mass dissolves completely in cold water, regenerating the original acid, which may again be decomposed by warming, reproduced by evaporation to dryness and re-solution, and so on indefinitely. This curious cycle of changes cannot fail to suggest some interesting questions to the student of chemical equilibrium. In no case is the total antimony of the solution present in the white precipitate, even when the latter is thrown down by prolonged boiling. A variable proportion of the metal always remains dissolved.

In order to determine the composition of the acid, a series of experiments, partly qualitative and partly quantitative, were undertaken. Theoretically, from the manner of its formation, it ought to be tartar emetic, with an atom of H in place of the atom of K. In other words, it should have the empirical formula $C_4H_5SbO_7$, a composition which is ordinarily represented by the rational symbol

$$C_4H_4O_6 \begin{cases} H \\ SbO. \end{cases}$$

As the acid could not be isolated in a definite anhydrous condition, because of its instability, indirect methods of examination had to be employed. To begin with, portions of it were respectively neutralized with the carbonates of potassium, barium, zinc, cobalt, and strontium, all of which dissolved freely. The portion treated with potassium carbonate gave readily crystals of tartar emetic, while that saturated with barium carbonate yielded the characteristic scales of the barium salt from which the acid itself is prepared. With cobalt and zinc carbonates, solutions were obtained which were perfectly clear when hot, but which solidified upon cooling to firm waxy or gelatinous masses. These were purified by re-solution and re-deposition, and dried at 100°. Upon estimating the cobalt and zinc, the percentages came out as follows, agreeing fairly with salts analogous to tartar emetic.

Cobalt salt	Co found, 9.88	Theory, 9.42
Zinc "	Zn " 11.10	" 10.11

Attempts to estimate the antimony in these compounds gave vary-

ing results, indicating that the formation of the absolutely pure salts probably depends upon undetermined conditions. The peculiar tendency of the acid to decompose, depositing its antimony, threw great difficulties in the way of preparing any but the most definite and stable of its derivatives. We have, in fact, strong reason to suspect that the carbonic acid evolved by its first action upon a carbonate, brings about a considerable change in its composition; but this point remains to be accurately settled. This suspicion was aroused by the peculiar action of the acid upon strontium carbonate. The solution thus obtained readily deposited rosettes of needles, which, dried by pressure between folds of filter paper, gave the following percentages of water, strontium and antimony. The analyses represent two distinct samples, prepared at different times and from different material.

	I.	II.
Sr	18.69	19.58
Sb	7.20	6.87
H_2O	...	21.90

It will be noticed that here, instead of an atomic ratio of Sr : Sb_2, the ratio is nearly Sr_1 : Sb. This agrees with no readily assignable formula, so that, although we have a clue to the real structure of the salt, we prefer to leave it for further investigation. Suffice it to say for the present that it is undoubtedly a double compound of a tartrate of strontium with a tartrate of strontium and antimony. Whether the latter is analogous to tartar emetic or not is still an open question. The formation of the salt evidently involves a partial decomposition of the acid and a deposition of some of its antimony.

Although the foregoing results with the salts of potassium, barium, cobalt and zinc were tolerably conclusive, another series of experiments was undertaken in order to ascertain whether, in the formation of the acid from the barium compound, the whole of the antimony passes into the filtrate. If it does, then the composition of the acid must be that which is theoretically assigned; if not, the questions involved are unsatisfactorily answered.

A quantity of the barium salt was prepared with every precaution needful to ensure purity, and the percentage of barium in it was accurately determined. The result agreed excellently with the formula of the compound. Several grams of this preparation, con-

taining obviously a known amount of antimony, were then suspended in ice-water and decomposed by an equivalent quantity of very dilute standardized sulphuric acid, added from a burette. After brief agitation the liquid was filtered into a stoppered cylinder containing lumps of ice, and the residue upon the filter was thoroughly washed with ice-water. The filtrate, which was perfectly clear at first but afterward deposited a small amount of sediment, was then diluted to a known volume and divided into five equal parts. In three of these the antimony was determined. The barium sulphate, however, retained a little antimony, a circumstance which could not be altogether avoided. If the sulphuric acid were added in the least deficiency, a part of the barium salt would remain upon the filter undecomposed; if in the smallest excess, a portion of the new acid would be destroyed; in no case could a trifling deposition of the white precipitate, prior to filtration, be absolutely prevented. This series of experiments was twice repeated. The first time, the filtrate contained about seven-eighths of the total antimony. On the second occasion the barium salt was first ground to fine powder in an agate mortar, and the results in the three portions of the filtrate examined were as follows. The figures represent the percentage of the total antimony of the barium salt which went through into solution.

92.62
93.98
92.96

Mean, 93.19

The variations in these values are due to the fact which is above mentioned, that the solution in the stoppered cylinder contained a slight deposit of white precipitate. This rendered it impossible to divide the acid into rigidly equal portions. The results, however, are as favorable as could be expected. The filtrate contains over nine-tenths of the total antimony; and this fact, together with that of the reproduction of the potassium and barium salts from the acid, fixes the empirical composition of the latter, in accordance with the formula $C_4H_5SbO_7$.

As an "acid tartrate of antimony" having the above formula is mentioned in many reference books, we undertook its re-examination in order to see whether it was identical with our acid. The compound in question is attributed to Péligot, who, however, gave no analysis of it. Upon mixing a solution of the hyperacid anti-

monious tartrate with alcohol he obtained a white precipitate which, after drying at 160°, consisted of $C_4H_5SbO_6$. This, dried at a lower temperature, ought to retain the elements of water, when it would be represented by the formula $C_4H_5SbO_7$. But this formula was not experimentally established. Accordingly we prepared the substance by Péligot's method, only we dried it at 100° instead of at 160°. Unfortunately, we did not get enough of the compound for complete analysis, but two estimates of antimony in it gave the following percentages:

39.27
39.41

Mean, 39.34

The compound $C_4H_5SbO_7$ should contain 42.10 per cent.; for $C_4H_5SbO_7 . H_2O$ the figure would be 39.60. Probably the latter formula is correct, although it needs scrupulous verification. At all events, Péligot's salt is not identical with our acid, for its solution is perfectly stable even upon long boiling. It is quite probable, therefore, though far from certain, that there are two isomeric bodies represented by the empirical formula $C_4H_5SbO_7$.

Upon studying the decomposition of the new acid by heat, highly satisfactory quantitative results were obtained. We have already stated that the white precipitate which is deposited upon warming does not contain the total antimony. No definite portion of the latter remains in solution, however, but a varying quantity, the amount depending upon undetermined conditions of dilution and temperature. Indeed, a part of the precipitate thrown down by actual boiling seems to redissolve upon cooling.

Evidently, the important thing to do was to ascertain the exact composition of this white precipitate. Accordingly, several lots of it were prepared, washed thoroughly, and dried at 100°. The product was a fine white powder, which, upon qualitative examination, proved to be a hydroxide of antimony, of decidedly stable character. Its water is retained even at 150°, and is completely expelled only at a much higher temperature. Its percentage of antimony was determined in two distinct samples and by two different methods. The results were as follows:

First sample	70.58	Weighed as Sb_2S_3
" "	70.45	" " Sb_2O_4
Second "	70.32	" " Sb_2S_3
Mean,	70.45	

A single estimation of water gave an amount corresponding to 1.83 per cent. of hydrogen. Taking oxygen by difference, we get the following composition for the white precipitate, which clearly establishes it as ortho-antimonious acid, $Sb(OH)_3$.

	Found.	Theory.
Sb	70.45	70.18
H	1.83	1.75
O	27.72	28.07
	100.00	100.00

Although ortho-antimonious acid is occasionally referred to upon theoretical grounds, we are unable to find that it has ever before been actually prepared and described. The only antimonious hydroxide of which authentic analyses have been published is that obtained by Schaffner, and to which the empirical formula $Sb_2H_4O_5$ has been assigned. This undoubtedly represents a hydrate of meta-antimonious acid, and may be formulated rationally as $2(SbO^-.OH).H_2O$. It contains 74.08 per cent. of antimony. The formation of the ortho-antimonious compound from our new complex acid is readily intelligible according to the subjoined equation,

$$C_4H_5SbO_7+2H_2O=SbH_3O_3+C_4H_6O_6.$$

Upon heating the mixture of hydroxide and tartaric acid thus obtained, the two molecules of water are eliminated, and $C_4H_5SbO_7$ is reproduced. We thus have a rational explanation of the curious cycle of chemical changes previously referred to.

As is well known, the addition of one of the stronger acids or alkalies to tartar emetic immediately produces a white precipitate. That which is thrown down by ammonia is said to be antimony trioxide, a fact which we have reverified. The precipitates formed by acids are ordinarily described as "basic compounds," containing both tartaric acid and the precipitant; but we cannot find that they have ever been systematically examined. In this direction we made a few experiments which, though by no means conclusive, suggest considerations different from those that are commonly entertained. We precipitated one portion of tartar emetic with sulphuric acid and another with nitric acid, and, after washing and drying, estimated the antimony in each precipitate. These are our results:

In the H_2SO_4 precipitate, 69.74 per cent.
" HNO_3 " 71.49 "

These figures are quite near the theoretical percentage of antimony in ortho-antimonious acid, and we are therefore inclined to regard both substances as that compound slightly impure. Each precipitate retained only traces of the stronger acid, and a quantity of organic matter which is easily ascribable to deficient washing. If our supposition is correct, the following equation will simply explain the formation of the $Sb(OH)_3$,

$$C_4H_4SbKO_7 + HNO_3 + 2H_2O = C_4H_6O_6 + KNO_3 + SbH_3O_3.$$

That is, the nitric acid takes away the potassium, forming a nitrate, and setting the new complex acid free. The latter, reacting with water, immediately displays its characteristic instability and undergoes decomposition, a part of the antimony remaining dissolved in the tartaric acid as usual. We have here an explanation of the fact which so puzzled some of the earlier theoretical chemists, namely, that a strong acid added to tartar emetic throws down only a portion, and that a variable portion, of the antimony.

The theoretical considerations suggested by the foregoing experiments are very obvious. We have found that tartar emetic yields an acid of definite constitution, which is certainly different from the acid tartrate of antimony described by Péligot. This acid deposits a hydroxide $Sb(OH)_3$, whereas if it contained an antimonyl group SbO we should expect to get from it meta-antimonious acid SbO . OH. Moreover, the liquid containing its deposit of ortho-antimonious acid readily regenerates the new tartrate in the peculiar manner described. We therefore change the old formula of acid antimonious tartrate,

$$C_4H_4O_6 \left\{ \begin{matrix} H \\ SbO, \end{matrix} \right.$$

into one representing our compound as derived from ortho-antimonious acid through the replacement of two univalent hydroxyl groups by the bivalent group $C_4H_4O_6$. Thus we have for ortho-antimonious acid, our new tartrantimonious acid and tartar emetic, the following formulae respectively:

$$Sb \left\{ \begin{matrix} OH \\ OH \\ OH \end{matrix} \right. \qquad Sb \left\{ \begin{matrix} C_4H_4O_6 \\ OH \end{matrix} \right. \qquad Sb \left\{ \begin{matrix} C_4H_4O_6 \\ OK. \end{matrix} \right.$$

All the other known tartrates of antimony, single and double, with possibly one exception, are capable of equally suggestive interpretations. Of course the remaining tartrantimonites, as we purpose calling the salts analogous to tartar emetic, are formulated

similarly to that familiar compound. The so-called neutral tartrate described by Berzelius is ordinarily written,

$$C_4H_4O_6 \begin{cases} SbO \\ SbO, \end{cases}$$

and its neutrality is assumed. It may with equal propriety be written thus, in comparison with antimony trioxide:

$$Sb_2 \begin{cases} O \\ O \\ O \end{cases} \qquad Sb_2 \begin{cases} C_4H_4O_6 \\ O \\ O. \end{cases}$$

The old view represents it as a neutral salt, while the new formula regards it as highly basic. Only experiment can decide which is the better.

The hyperacid tartrate of antimony described by Péligot is commonly regarded as formed by the union of one molecule of the acid tartrate with one molecule of tartaric acid, thus:

$$C_4H_4O_6 \begin{cases} H \\ SbO \end{cases} . C_4H_6O_6.$$

We ignore water of crystallization. It may also be written as follows:

$$Sb \begin{cases} C_4H_5O_6 \\ C_4H_5O_6 \\ OH. \end{cases}$$

For this formula we at once find a justification in Knapp's acid tartar emetic, $C_4H_4K(SbO)O_6 . C_4H_6O_6$. This becomes

$$Sb \begin{cases} C_4H_5O_6 \\ C_4H_5O_6 \\ OK. \end{cases}$$

Here then we have a new complex acid derived from ortho-antimonious and tartaric acids, and also its potassium salt. If this view is correct, a new line of investigation is opened up among the tartrates of antimony, and we may reasonably expect to discover a series of compounds analogous in constitution to the well-known glycero-tartaric acids. For example, glycero-ditartaric acid may be written as follows:

$$C_3H_5 \begin{cases} C_4H_5O_6 \\ C_4H_5O_6 \\ OH. \end{cases}$$

This acid, however, is dibasic, whereas the corresponding antimony compound should have a basicity of three. Such differences are naturally to be anticipated, since antimony is a feebly electro-nega-

tive metal, while glyceryl is a distinctly electro-positive group. Ortho-antimonious acid and glycerine, therefore, although peculiarly comparable, are so only within certain limits. The hydroxyl molecules of the one must have different functions as regards basicity from the similar molecules of the other.

By heating the tartrates of antimony to temperatures near 160°, certain compounds are produced, of which the formation may be represented as follows. In no case is the SbO group necessary.

$$Sb_2 \begin{cases} C_4H_4O_6 \\ O \\ O \end{cases} - H_2O = Sb_2 \begin{cases} C_4H_2O_6 \\ O. \end{cases}$$

$$Sb \begin{cases} C_4H_4O_6 \\ OH \end{cases} - H_2O = SbC_4H_3O_5.$$

$$Sb \begin{cases} C_4H_4O_6 \\ OK \end{cases} - H_2O = SbKC_4H_2O_6.$$

In two of these bodies we encounter the residue $C_4H_2O_5$, of which the best known representative is the tetrabasic lead tartrate. In the other, the trivalent antimony directly replaces three of the hydrogen atoms of tartaric acid. The one compound which we are as yet unable to formulate intelligibly is that described by Knapp as formed from the union of a molecule of tartar emetic with three molecules of acid potassium tartrate. This compound, however, needs careful verification.

Although in all the actually known tartrates of antimony the SbO group is, as we have said, superfluous, there may yet be discovered salts in which it can have a definite existence. For example, we have seen that there may be two isomers bearing the formula $C_4H_3SbO_5$. One of these, our tartrantimonious acid, we have definitely established as an ortho compound. The other, if its existence should be verified, would probably turn out to be a meta-antimonious derivative, containing the meta-group SbO. This supposition suggests that there may possibly be two isomeric series of antimonious tartrates, and points out a wide field for future research.

In conclusion, it is hardly necessary to say that the reasoning which we have applied to the tartrates of antimony applies also to the corresponding compounds of boron, arsenic, chromium, and ferric iron. Each of these elements forms with tartaric acid and potassium, salts analogous to tartar emetic, which are commonly represented as containing radicles similar to the group SbO. These

radicles we may now reject, and formulate all such compounds as derived from complex acids constructed upon the tartrantimonious type. That these formulae are simpler, clearer, and less hypothetical than the old symbols, we think there can be no doubt.

XVI.—ON THE RELATIVE STABILITY OF CERTAIN ORGANIC SALTS.

By Miles Beamer and F. W. Clarke.

The barium salts of methylsulphuric acid and its homologues, each containing two molecules of water of crystallization, and all yielding comparable products upon decomposition by heat, afford a very good series for the study of relative stability. Decomposition begins at comparatively low temperatures, proceeds slowly and regularly, and its rate differs with the several compounds.

In our experiments the methyl, ethyl, propyl, isopropyl, isobutyl, and amyl salts were studied. Two grams of each were placed in porcelain crucibles, and heated side by side in an air-bath; so that all were simultaneously exposed to identical conditions of temperature. The source of heat was a gas-flame, controlled by a Bunsen-Kemp regulator. Every set of experiments consisted of several successive heatings; after each one of which the salts were allowed to cool, and their losses of weight were determined. In all, nine series of experiments were made. The first was a set of half-hour heatings through a range of gradually increasing temperatures, and served only for preliminary control. Series two and three were half-hour heatings at 100°, continued until no farther loss of weight ensued. Series four, five, six, seven, and nine were of hour heatings at 100°, while series eight consisted of hour heatings at 110°. In each case heating was continued until for the given temperature the weight of the salts became constant.

In order that our results may be fairly comparable we have expressed our percentages of loss after a somewhat peculiar manner. Each salt, when strongly ignited, leaves barium sulphate, and loses certain volatile products; which, in the case of the amyl compound, amount to 45.96 per cent. of the whole. In each case this total possible loss, which differs with the different salts, is taken as our

standard, instead of the actual weight of the substance employed, and to it our percentages are referred. Fifty per cent., therefore, in our computations, means not half of the salt under examination, but half of the quantity which it is capable of losing upon ignition.

The general average of our results for all the heatings made through one hour at 100°, is given in the following table. The numbers in the first column indicate the successive heatings. In the other columns are stated the percentages of loss for the respective compounds, expressed according to the method explained above.

No.	Amyl Salt.	Isobutyl Salt.	Propyl Salt.	Isopropyl Salt.	Ethyl Salt.	Methyl Salt.
1.	18.41	29.69	19.19	42.14	35.22	29.74
2.	35.55	46.88	42.27	43.52	43.33	39.34
3.	41.90	53.10	43.08	44.97	47.86	41.22
4.	58.89	57.38	49.49	45.60	51.16	43.17
5.	65.43	59.81	50.92	46.51	55.60	45.56
6.	69.38	61.99	54.25	47.61	58.33	

It is plainly evident that these figures have no absolute significance, but only a comparative value. They show that at the temperature under consideration the amyl salt has the widest range of loss, and that its decomposition proceeds the most regularly. The isobutyl salt comes next in these particulars, and is followed in proper order by the propyl, ethyl, methyl, and isopropyl compounds. If we consider the maximum losses only, then the order will be the same, except that the ethyl and propyl salts will change places. In short, we may safely infer from the data before us, that with the compounds of higher molecular weight, decomposition begins more slowly, but proceeds farther, than with the lower salts of the series. The isopropyl compound, however, acts somewhat abnormally; losing but little after the first heating. Its rapidity of loss is therefore relatively great; while its range of loss is comparatively small. It would be interesting to compare the isobutyl salt with its normal analogue, but for this purpose material failed us. We prepared a small quantity of the normal alcohol, but could not secure enough to work with.

No attempt was made to determine the effect of mass upon rate of change. Investigations in that direction must be left for some future time.

XVII.—SOME NEW SALTS OF URANIUM.

By F. W. Clarke and Mary E. Owens.

Sodium uranate dissolves readily in the substituted acetic acids, yielding definite salts analogous to the well known sodio-uranic acetate.

Sodio-uranic monochloracetate forms large sulphur yellow prisms containing two molecules of water. The analysis agrees well with the formula $NaC_2H_2ClO_2.2(UO.C_2H_2ClO_2).2H_2O$. Sp. gr., 2.748 at 14°.

		Found.		Theory.
U	39.39	39.49	39.76	39.25
Na	3.95	3.78	3.83	3.74
H_2O	5.83			5.88

The dichloracetate and monobromacetate, like the ordinary acetate, are anhydrous. Both salts form small yellow crystals, those of the monobromacetate being clustered in regular stellate groups. Analytical results are as follows:

Dichloracetate, $NaC_2HCl_2O_2.2(UO.C_2HCl_2O_2)$.

	Found.		Theory.
U	36.15	35.69	35.34
Na	3.47	3.49	3.39

Monobromacetate, $NaC_2H_2BrO_2.2(UO.C_2H_2BrO_2)$.

	Found.		Theory.
U	34.22	33.47	33.85
Na	3.28	3.36	3.24

A solution of the double trichloracetate was prepared, but it dried up to a gummy mass without yielding any crystals.

XVIII.—GRAPHITE FROM DUCKTOWN, TENNESSEE.

By W. L. Dudley and F. W. Clarke.

About two years ago we received from the Ducktown Copper Mine a large mass of mineral which purported to be molybdenite.

Upon examination, however, it proved to be merely graphite, mixed with copper pyrites and various silicates. As graphite has never before been discovered in that locality, and as the occurrence of the mineral in such associations is somewhat unusual, we have thought it worth while to put the fact on record. The purest sample we could find gave us 67.99 per cent. of carbon, and 32.01 of ash. The ash had the following composition:

SiO_2	41.06
Fe_2O_3	26.69
Al_2O_3	20.37
CaO	9.76
MgO	2.04
CuO	trace
Mn_2O_3	"
	99.92

This is nearly an impure iron epidote, the oxygen ratios being approximately $RO : 2R_2O_3 : 3SiO_2$.

ON THE DISTRIBUTION OF ARSENIC IN THE HUMAN BODY IN A CASE OF ARSENICAL POISONING.

By S. W. Johnson and R. H. Chittenden.

A recent case of suspected arsenical poisoning in the State of Connecticut led the proper authorities to demand a chemical examination of the body of the victim, Mrs. Riddle. Accordingly the body, which had been buried nearly a year and a half, was disinterred, and all the internal organs removed separately and placed in sealed glass bottles. The entire body was found in a good state of preservation, and the mucous and other tissues, as well as the different organs, showed a firmness and consistency seldom seen in a body so long buried. On opening the stomach the lining membrane was found quite entire, though naturally much shrunken, while adhering to it was found a quantity of a black substance,

which, on examination, proved to be bismuth sulphide, formed probably from bismuth subnitrate, which entered into the composition of a medicine taken by the deceased. Portions of this membrane, freed from all adhering matter by thorough washing with water, showed, scattered over its surface, brownish black stains of bismuth sulphide, while here and there were to be seen yellow stains soluble in ammonia, which, on later examination, proved to be arsenious sulphide. The liver and intestines, which in many places had the appearance of fresh organs, likewise showed the yellow stains, and these, together with the remainder of the internal organs, contained an appreciable quantity of arsenic. As the total quantity of arsenic found at this time (2.3798 grains As_2O_3) was, according to the theory of the defense, within the possible limits of a non-fatal dose to a person accustomed to the use of arsenic, the prosecution ordered a second disinterment, and such a thorough chemical investigation to be made as would show with accuracy the total amount of arsenic contained in the entire body. Accordingly, at the second disinterment, such a dissection was made as would insure a fair estimate of the entire content of arsenic. Twenty-one pounds of tissue from different portions of the body were taken, and each individual part subjected to a separate analysis. The entire body, after the removal of the soft organs, weighed but $55\frac{1}{2}$ pounds, so that nearly one-half of the solid tissue of the body was taken for examination. The method of analysis employed was the one recently described by Chittenden and Donaldson;* a method which allows of the accurate determination of minute quantities of arsenic, and in which the arsenic is weighed in the metallic state. 100 grams of sampled substance were employed for each determination, except in several cases where the amount of arsenic was found to be quite small, and then larger quantities were taken; thus in the brain 300 grams were employed. The sampling of the larger masses of bone and muscle tissue, as well as the small organs, was accomplished by placing the entire portion in a small quantity of nitric acid for several days, which gradually disintegrated it, and afterwards by the aid of a gentle heat speedily reduced it to a thin, pasty mass, capable of being accurately sampled. From the amount of arsenic found in the 100 grams of sampled matter, the content of the entire organ or portion of tissue was calculated.

* This Journal, vol. 2, p. 235.

Internal Organs.

Substance.	Total Weight.	As_2O_3 Found.	Percentage of As_2O_3.
Stomach and Spleen	514 grams	.05359 gram	.01040 per ct.
Kidneys	80 "	.00660 "	.00825 "
Liver	590 "	.04788 "	.00811 "
One Lung and Heart	441 "	.01454 "	.00329 "
Intestines and Uterus	978 "	.02582 "	.00260 "
One Lung and Liquid from Thorax	402 "	.00583 "	.00140 "
Urinary Bladder, etc.,	73 "	distinct trace	
Brain	477 "	unweighable trace	
	3555 "	.15426 gram	.00433 "
	7 lb. 13 oz., 173.40 grains	2.3805 grains	

Left Arm.

Substance.	Total Weight.	As_2O_3 Found.	Percentage of As_2O_3.
Upper Arm	665 grams	.00542 gram	.00081 per ct.
Fore Arm	288 "	.00158 "	.00055 "
Hand	150 "	.00019 "	.00012 "
	1103 "	.00719 "	.00065 "
	2 lb. 6 oz., 396.71 grains	.11120 grain	

Right Leg.

Substance.	Total Weight.	As_2O_3 Found.	Percentage of As_2O_3.
Leg from Knee to Ankle	1323 grams	.00864 gram	.00065 per ct.
Flesh from Thigh	3160 "	.01635 "	.00051 "
Foot	468 "	.00105 "	.00022 "
Thigh Bone	615 "	.00040 "	.00006 "
	5566 "	.02644 "	.00047 "
	12 lb. 4 oz., 146.84 grains	.40815 grain	

Muscle and Bone Tissue from other parts of the Body.

Substance.	Total Weight.	As_2O_3 Found.	Percentage of As_2O_3.
Transverse section of body above Pelvis	1920 grams	.03011 gram	.00156 per ct.
Muscle and Ribs from left Breast	406 "	.00371 "	.00091 "
Abdominal Muscle, right Side	615 "	.00358 "	.00058 "
	2941 grams	.03740 gram	.00127 "
	6 lb. 7 oz., 324.24 grains	.57715 grain	

Summary of the Examination of Tissue.

	Total Weight.	Total As_2O_3.
Arm	2 lb. 6 oz., 396.71 grains	.11120 grain
Leg	12 lb. 4 oz., 146.84 "	.40815 "
Muscular and Bony Tissue from other parts of the body	6 lb. 7 oz., 324.24 "	.57715 "
	20 17 867.79	1.09650
	21 2 430.29=339 oz.	

The entire body, aside from the internal organs, weighed at the second interment, 55½ pounds=880 oz. Thus the proportion,

339 : 880 : : 1.09650 : 2.8463 grains,

gives with reasonable accuracy the total amount of As_2O_3 contained in the body tissue, and this amount added to that contained in the internal organs, gives a total of 5.2261 grains As_2O_3. In the stomach and spleen were found an amount of bismuth corresponding to .26648 gram of bismuth teroxide; which, on the supposition that bismuth subnitrate has the composition $BiNO_4+H_2O$, would correspond to 5.3842 grains of the latter. In the liver only an unweighable trace of bismuth was present.

A backward glance at the data already given enables us to see that the distribution of the arsenic is such as could result only from a case of chronic poisoning. The small but still weighable quantity found in the bones, and the regular distribution of the arsenic through all parts of the muscular tissue, are ample evidence of this fact. It is perhaps worthy of notice that the 55½ pounds of tissue contain more of the arsenic than all the internal organs. Many investigators have called attention to the absorption of arsenic by the muscle tissue, and the localization of arsenic in the muscles has long been accepted as a settled fact; but recently Scolosuboff,* under the guidance of Gautier, has attempted to show that arsenic, instead of localizing itself pre-eminently in the muscles, is specially absorbed and retained by the nerve tissue. The experiments upon which Scolosuboff based his conclusions were made upon animals poisoned with a solution of sodium arsenite, fed to them with their food; thus a bull-dog having taken during 34 days doses of As_2O_3 in the form of sodium arsenite, increasing from .005 gram to .150 gram per day, yielded the following results:

* Bulletin de la Société Chimique de Paris, 24, 124.

100 grams	fresh	muscle	.00025	gram	metallic arsenic
"	"	liver	.00271	"	" "
"	"	brain	.00885	"	" "
"	"	marrow	.00933	"	" "

Scolosuboff also states that the results are still more striking in cases of acute poisoning. Thus he found that by injecting .15 gram of sodium arsenite under the skin of a bull-dog weighing 11 kilograms, death was induced in 17 hours; and while the arsenical mirror from the brain was very strong, it was less from the marrow, and scarcely visible from the liver and muscle. In another experiment, a griffin dog of the same weight received 10 grams of As_2O_3 in the form of arsenite, by injection into the cellular tissue. The animal died in $17\frac{1}{2}$ hours. 100 grams of brain substance yielded a mirror of metallic arsenic weighing .00117 gram. The ring from 200 grams of liver, though plainly visible, was not weighable, while that from the muscles was almost invisible. Scolosuboff therefore draws the conclusion that arsenic is specially localized in the nerve tissue of the poisoned animal, and that in cases of acute poisoning the legal expert has need of searching for the metal specially in the brain of the victim; the liver, contrary to the usually accepted idea, when the action has been rapid, frequently not containing any of the poison. Such experiments as the foregoing, however, appear to our minds wholly valueless for toxical purposes, and the conclusion drawn from them very misleading. It is a well-known fact that the form of the poison modifies very decidedly the rapidity of its absorption, and it is quite probable that the form in which the poison is introduced may modify the rate and amount of absorption by different organs and tissues. And again, the period of time elapsing between the last dose of arsenic and the death of the animal, or, in other words, the length of time in which elimination has been going on since the last dose was given, may modify the results considerably, especially in the case of such a soluble combination as sodium arsenite, in which both absorption and elimination would naturally go on with rapidity. Cases of poisoning by solution of sodium arsenite are not of common occurrence compared with the number of those produced by the more insoluble white oxide, and deductions drawn from the experiments of Scolosuboff are not applicable to the common forms of arsenic poisoning, as is evidenced by the facts.

In the examination of the body of Mary Stannard,* where death was supposed to have taken place shortly after the introduction of the poison, one of us (J.) found 83.23 grains of arsenious oxide in the stomach, liver, and other internal organs, while the brain contained a hardly perceptible trace of arsenic; and in the examination of the body of Mrs. Riddle, 100 grams of abdominal muscle gave .00045 gram of metallic arsenic; 100 grams of muscle and ribs .0097 gram of metallic arsenic, and 100 grams of muscle from thigh .0004 gram of metal, while 300 grams of brain yielded an unweighable mirror.

An experiment conducted here in the laboratory on a large coach-dog gave the following results: 6.5 grams of solid As_2O_3 were given to the dog with meat during a period of 8 days in doses increasing from .1 gram to 2.5 grams per day. 24 hours after the last dose was given the dog was killed and examined.

100 grams of intestines	gave	.0020 gram	metallic arsenic
100 " liver	"	.0010 "	" "
113 " kidneys	"	.0005 "	" "
100 " muscle	"	.0002 "	" "
150 " urine in bladder	"	.0003 "	" "
Entire brain	"	faint mirror	" "
100 grams of blood	"	distinct mirror	" "

Thus it appears that in this case, as in the toxical cases quoted above, the amount of arsenic absorbed by the brain matter is very small compared with the amount absorbed by other tissues. In a very recent article on the distribution of arsenic in the animal body after the taking of arsenious oxide, E. Ludwig† finds by constantly agreeing results, that in the case of human beings as well as dogs poisoned by arsenic, both in acute and chronic cases, the liver contains the most arsenic; in acute forms the kidneys contain an abundant quantity; while the bones and brain, in either case, contain only a very small trace.

NEW HAVEN, *October* 4, 1880.

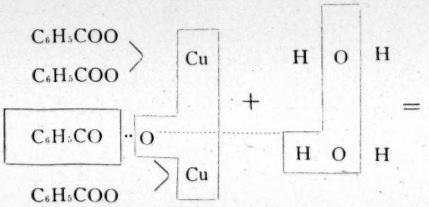
*Murdered, after administration of arsenic, by severing the blood-vessels of the neck, September, 1878.

†Anzeiger der K. Akad. d. Wissensch. Wien, No. 18, p. 18; also abstract in Jahresbericht Thier Chemie für 1879, p. 85.

SYNTHESIS OF SALICYLIC ACID.

By Edgar F. Smith.

Upon heating 1 part of copper benzoate with about 3 parts of distilled water in a sealed tube at a temperature of 180° C., for a period of three hours, a large quantity of cuprous oxide separated. The contents of the tube were then removed to a rather large beaker, acidulated with hydrochloric acid, and the solution supersaturated with hydrogen sulphide. The filtrate from the copper sulphide contained, of course, a considerable amount of benzoic acid, which was removed by distillation in a current of steam. The residual liquid reduced to a small volume gave a crystallization of needles, fusing constant at 156° C., and afforded with ferric chloride the characteristic coloration given by salicylic acid. The salts also proved the presence of the latter. The reaction, then, described above may be graphically represented as follows:



$$Cu_2O + 3C_6H_5.COOH + C_6H_4OH.COOH.$$

Salicylic Acid.

The experiment repeated gave the same result. A quantity sufficient for analysis was obtained, although its separation from the benzoic acid was attended with difficulty. In one or two instances the method was slightly modified. An aqueous solution of benzoic acid and an ammoniacal solution of cupric oxide were employed. The mixture was heated as usual, but it was necessary to increase the temperature to 220° C. The yield of salicylic acid in either case was never very abundant

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REVIEWS AND REPORTS.

Recent Progress in Agricultural Science.

The objects of agriculture may be briefly summarized as the production of certain plants and animals useful to man. It is the office of agricultural science to investigate and expound the chemical, physical and biological laws upon which this production depends, while the art of agriculture consists in the application in practice of the principles revealed by the study of the science. Corresponding to the two objects of agriculture just mentioned, we may logically consider agricultural science under the two heads of Vegetable Production and Animal Production, taking up under each one, first, the laws of vegetable or animal production in general, and second, the conditions under which such production is actually carried on.

Vegetable Production.

Physiology and Bio-chemistry of the Plant.

Germination.—The first act in the life of the plant is the germination of the seed from which it grows. The chemical changes taking place during this process are so similar to those which are continually going on in the mature plant that they may be conveniently considered in that connection, while here we take up briefly some of the recent contributions to our knowledge of the *conditions of germination*. These conditions are, in general, a proper temperature and the presence of sufficient moisture and oxygen.

Effect of Temperature on the Vitality and Germination of Seeds.—Numerous observations on these points have been made within a few years, with the purpose of ascertaining the limits of temperature within which germination is possible, and also within which seeds can retain their vitality.

The observations on the former point have been, in general, confirmatory of those of Sachs, though the minimum temperature at which germination can take place seems to be somewhat lower than is stated by that observer.

Thus Uloth* observed plants of wheat and of a species of maple, the seeds of which had been introduced into an ice-cellar along with the ice and had there germinated, and developed plants whose roots had penetrated the ice to a distance of, in some cases, over 16 cm. The germination must have taken place at a temperature little, if any, above 0° C., and as no cracks were observed in the

* Jahresber. Agr. Chem. 13-15, II, 99.

ice, it would seem that the heat developed by the chemical changes going on in the seedlings was sufficient to enable the roots to *melt* their way through the ice.

Kerner* experimented on the seeds of alpine plants, placing them in soil contained in glass tubes which were sunk in the water of certain cold springs whose temperature was practically constant at +2° C., and found them capable of germination under these circumstances. Kerner also states that many alpine plants not only germinate but grow and blossom under the snow and ice, penetrating the latter in the same manner as the roots of the wheat and maple observed by Uloth.

Haberlandt,† in some earlier experiments, found the minimum temperature for the germination of most seeds to lie between 3.8° and 8.4° C. Uloth's observation led to experiments on the effect of a temperature of 0°C. in germination. The experiments were made in a specially constructed ice-chest, on a large variety of seeds, with results differing somewhat from those noticed by Uloth. It was found‡ that out of twenty-five kinds of seeds, including those of the most important agricultural plants, sixteen, among which may be mentioned wheat, barley, oats and buckwheat, did not germinate at all; four, viz., rye, hemp, vetches and peas, did not pass beyond the first stages of germination; while mustard, *Camelina sativa*, Swedish clover (*Trifolium hybridum*), red clover, and lucerne showed a decided growth of the radicle. Nearly all the seeds of rye, about half those of the lucerne, 14 per cent. of the hemp, 17 per cent. of the mustard, and 10 per cent. of the red clover germinated. Haberlandt believes that the seeds capable of germinating at such a low temperature would yield plants needing for their development a less amount of heat than those growing from seeds of the same kind not capable of thus germinating, and that it might be possible in this way to produce early ripening or hardy varieties.

The same author has experimented on the germination of the seeds of tropical plants,§ and has found, as was to be expected, that the minimum temperature for the germination of these seeds is considerably higher than for the seeds of plants inhabiting colder latitudes, ranging from 10° to 15° C. It is worthy of note in this connection that the maximum temperature for these seeds was not essentially higher than for many plants which have become naturalized in temperate latitudes, while the minimum temperature is in many cases considerably higher. Haberlandt considers it as highly probable that, as a rule, those plants which are most widely distributed north and south are able to germinate at the most diverse temperatures.

The maximum temperature at which germination takes place varies considerably with different species, being in some cases as low as 20° C. and seldom rising above 40° C.

The *vitality* of seeds is retained through a range of temperature

* Jahresber. Agr. Chem. 16-17, I, 259.
† Landw. Versuchs-Stationen, 17, 104.
‡ Wissenschaftlich-prakt. Untersuch., 1, 113.
§ Ibid. 1, 117.

much exceeding that within which germination is possible. Dry seeds appear to be capable of withstanding quite low temperatures, while if previously soaked in water they are much more sensitive, as has been shown by Haberlandt* and by Detmer.† Haberlandt exposed seeds to the temperatures of —10° C. and —24° C.; he found that the former temperature diminished the germinative power less than the latter, that dry seeds suffered less than soaked ones, that quick thawing produced less injury than slow, and that those seeds which contained much oil were best able to withstand cold. The same experimenter‡ has observed a curious effect of cold on flax. Soaked seeds of flax were exposed to a temperature of —17.5° C., were then slowly thawed, and sown as usual. The resulting plants showed an abnormal length of stem as compared with plants grown from the unfrozen seed, exceeding them by 39-45 per cent. in this respect. No further experiments confirmatory of this remarkable result have yet been reported.

The highest temperature which seeds can bear without losing their vitality seems to depend largely on their state of dryness, though differences are observed between different species and different individuals of the same species. Thus Just§ found that clover seeds were killed at a temperature of 75° C. in an atmosphere saturated with water, and even at 50° C. did not survive for 48 hours, while dry seeds withstood temperatures below 120° C., though they germinated more slowly afterwards.

So, too, Haberlandt‖ found that soaking seeds in water of 40° to 50° C. diminished or destroyed the vitality of most seeds, and that even 30° C. was very injurious to some seeds, while v. Höhnel¶ found that most seeds endured a temperature of 110° C. for an hour, if they were sufficiently dry (3 per cent. or less of water).

The fact of seeds withstanding the action of boiling water for some time, which has frequently been observed, is attributed by Haberlandt to the resistance of the outer coats of the seed to the water, which is thus prevented from reaching the interior of the seeds.

The length of time during which seeds are exposed to a high temperature is also an important factor in determining the result. In general, the higher the temperature and the moister the seed or the surrounding air, the sooner is the vitality destroyed. In some later experiments Just** has found that the vitality of some seeds is impaired by the action of moist air at ordinary temperatures, and Haberlandt, in his last cited paper, states that the germinative power of oats and barley is diminished by soaking in water at ordinary temperatures. Other seeds suffer no perceptible injury by such treatment; but as the temperature to which they are exposed is raised they lose their germinative power more and more quickly, until a temperature is reached which destroys it at once, or as soon as the seed has time to become heated through.

* Jahresber. Agr. Chem. 16-17. I 263. † Forschungen Agr. Phys. 11, 60.
‡ Landw. Versuchs-Stationen, 21, 357. § Jahresber Agr. Chem. 16-17, I, 258.
‖ Wiss. prakt. Untersuchungen, 2, 47. ¶ Ibid 2, 77.
** Jahresber. Agr. Chem. N. F. 1, 224.

It would seem that all seeds lose their vitality after a certain unknown (and probably long) time, and that the action of heat and moisture is simply to accelerate the processes which in any case lead in time to the death of the seed. In accordance with this view, Just (*loc. cit.*) found that exposure of seeds to a heat insufficient to kill them produced much the same effects as long storing, the seed germinating more slowly and feebly, as is the case with old seed.

Presence of Oxygen.—The presence of oxygen, as is well known, is essential to germination, and recent experiments by Haberlandt* go to show that in some cases the oxygen which is inclosed in the seed itself is necessary to initiate the germination. This observer experimented on seeds out of which the air had been pumped (the seeds being placed under water in the exhausted receiver of an air pump), and found that while in most cases no decided effect was observable, seeds of the oat, beet and fiesole were either incapable of germination, or that a far smaller percentage of them germinated than was the case without this treatment.

A certain dilution of the oxygen is also necessary. Böhm† has found that seeds are not able to get beyond the first stages of germination in pure oxygen at the pressure of the atmosphere, but that diminishing the pressure to about 150 mm. of mercury, either by dilution with hydrogen or by attenuation by means of the air pump, enables the germination to progress normally.

Too great dilution of the oxygen appears to be equally fatal. Bert‡ found that diminishing the pressure of the air in which the seeds were placed retarded their germination, and that the latter ceased entirely at a pressure of from 4–10 cm. of mercury, though the seeds retained their vitality. He ascribes the result to the decreased supply of oxygen consequent on the diminished pressure. On the other hand, he found that a pressure of 2 or 3 atmospheres slightly accelerated the germination, but that one of 4–5 atmospheres hindered it and a higher pressure stopped it. This result he ascribes to the too great density of the oxygen.

Finally, Cossa§ has found that nitrous oxide cannot take the place of oxygen. He found that while the seeds of wheat and maize used by him germinated in two days in air or oxygen, no signs of germination were to be seen after twelve days in those placed in nitrous oxide.

H. P. ARMSBY.

A THEORETICAL AND PRACTICAL TREATISE ON THE MANUFACTURE OF SULPHURIC ACID AND ALKALI, WITH THE COLLATERAL BRANCHES. By George Lunge, Ph. D., F. C. S., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich, (formerly manager of the Tyne Alkali Works, South Shields.) Vols. I and II. Van Voorst, London, 1878 and 1880.

This book, of which the first two volumes have now appeared, well deserves notice as a good example of a first-class monograph

* Wiss. prakt. Untersuchungen, 1, 104.
† Jahresber. Agr. Chem. 16–17, I., 258.
‡ Jahresber. Agr. Chem. 16–17, I, 260.
§ Landw. Versuchs-Stationen, 18, 60.

treatise in the field of chemical technology. It proposes to describe in full, for the student and for the manager of works, the great group of allied manufactures which includes the production of sulphuric and hydrochloric acids, sodium sulphate, carbonate and hydrate, chlorine, bleaching powder, and their minor associates. The plan is admirably carried out for sulphuric acid, for soda by the Leblanc process, and for all minor products immediately dependent upon these, in the portion of the work already published, and doubtless will be brought to a handsome conclusion in the third volume, announced as soon to appear, in which the other processes of soda manufacture, chloride of lime and potassium chlorate, are to be treated.

The general arrangement of the large mass of material at the disposal of the author is clear and logical—material drawn from ample study of the literature of the subject, from personal experience in the direction of the principal forms of manufacture described, and from visits to and correspondence with many analogous works in England and on the continent of Europe.

Historical sketches of the rise and progress of the industries in question are given at the beginning of the various divisions of the work, and these, although brief and condensed, are sufficient for the most part in view of the main purpose of the book.

Good judgment is shown in the proportionate space allotted to different processes and modifications of practice, and in the criticism of these, and statement of the balance of advantages and defects which they exhibit, a fair and impartial spirit is observable. This is well illustrated by the discussion of the salt-cake process of Hargreaves in contrast with the use of the improved forms of sulphate furnace employing sulphuric acid. In a few instances one may doubt whether full justice has been done to a particular invention, as in the case of Sprengel's water-spray jet for the oil of vitriol chambers, the advantage of which, in giving control over the working temperature, does not seem to be sufficiently recognized; but this bears with it no appearance of partisanship. It is noteworthy that differences of English and Continental practice, or of usage in different districts, receive equal attention, as, for instance, the supply to the vitriol chambers of nitric acid in liquid form or in the state of vapor from nitre pots, the concentration of sulphuric acid in platinum or in glass vessels, the condensation of hydrochloric acid in stoneware jars or in coke-towers, etc.

Due notice is taken of improvements or variations of practice proposed, but not brought into use, while space is not wasted by over-lengthy discussions of methods incapable of being or very unlikely to be made of any real use. More attention is given to the progress already made with partially successful improvements, such as the utilization for the manufacture of sulphuric acid of sulphur dioxide from roasting of blende, copper and lead mattes, etc., than to desiderata still remaining to be supplied. Under this latter head it would seem that good results might be looked for from sys-

tematic research on the alloys of lead, with a view to diminishing the corrosion of the surface of the vitriol chambers; the value in this direction of a little antimony in the lead seems to be established, but whether the addition of some determinate amount of this alloy, or the use of some other metal with it or instead of it, might not give much better results seems worthy of further examination.

The general course of processes actually in use on the large scale is fully and clearly described, including of course all the more recently developed methods, such as the working of the Glover tower, (the importance of which in de-nitrating and concentrating sulphuric acid is strongly urged), the Hargreaves and Robinson process for making salt-cake by the direct use of sulphur dioxide from the burners, Mactear's mode of introducing surplus lime in the black-ball furnace, with the modifications subsequently made by Pechiney and Weldon, the production of caustic soda from tank-liquor, the improved form of Schaffner and Helbig's process for the recovery of sulphur from tank-waste, etc. The minute points of practical detail which so often distinguish a mere project or suggestion from a workable process are dwelt upon with due emphasis, and much useful experience is embodied in the comparison of practice at different factories. No allusion is to be found to the curious belief or superstition, whichever it may be, prevailing widely, it is said, among makers of sulphuric acid in this country, to the effect that Sicilian sulphur imported in old petroleum barrels, or as some claim, even in ships which have previously had a cargo of petroleum, burns with difficulty, requiring constant raking to keep it on fire, or a covering of sand on the burner to retain the heat. Even those who disclaim a belief in the alleged effect are in the habit of inserting a clause in their ship-charters against contact with petroleum.

Minor processes, not in general use, but employed at some works only, are not neglected, such as the purification of sulphuric acid by removal of arsenic, the industrial production of sulphur trioxide, and the like.

Mechanical and constructive appliances of all kinds, old and new, are described, and their several merits and defects considered; thus suitable space is devoted to the more recent forms of burners for pyrites in dust or small fragments, such as those of Hasenclever, Gerstenhöfer, Malétra and Schaffner; to various forms of acid pumps; to Faure and Kessler's stills of combined lead and platinum, and the newer forms of simple platinum stills for sulphuric acid concentration; to mechanical salt-cake furnaces, and to black-ash furnaces with revolving hearths.

Separate chapters are occupied with the theory of the more important and complex processes, and our present knowledge of the gaseous reactions occurring in the oil of vitriol chambers, of the changes brought about in the black-ash furnace, etc., is fairly presented. It is to be noted that Witt* has recently endeavored to

* Chemisches Central-Blatt, 14 April, 1880, S. 226.

show that nitrogen trioxide, N_2O_3, which Lunge assumes to be the oxide of nitrogen most largely present in the atmosphere of a normally working lead chamber, does not exist as such in the gaseous state, but splits at the moment of its production into a mixture of the dioxide and tetroxide. In evidence of this, Witt states that N_2O_4, which he views as nitrosyl nitrate, if conducted into a carefully dried solution of aniline in benzole, gives rise to the production of diazobenzol nitrate, and that if N_2O_3 be similarly treated, the same diazobenzol salt is formed and colorless NO is given off.

The methods of analysis applicable to the technical examination of the various materials used and products obtained are noticed, and various simple forms of apparatus for gaseous and liquid volumetric work are described. Results of the author's own experiments are occasionally given.

Sufficiently full accounts are given of the means of working up and utilizing by-products, as, for instance, the extraction of copper and silver from burnt pyrites.

Estimates of the cost of the more important processes are presented, and full estimates of the cost of plant are promised for the concluding volume. Under the head of yield obtained from given quantities of material, it is estimated that a very good average result of the Leblanc soda process in British alkali works will not show more than about 85.5 per cent. of the amount of product indicated by theory. In connection with one of the minor elements of cost in vitriol making, namely the loss of platinum dissolved by the acid from the stills, the statement is repeated which has appeared for the last few years, that this loss occurs with sulphuric acid quite free from the oxides or acids of nitrogen; but Scheurer-Kestner, the original authority on this subject, who has probably given to it more attention than any one else, has lately * claimed that perfectly pure sulphuric acid does not attack platinum, while extremely minute traces of the nitrogen compounds, easily overlooked in the application of ordinary tests, render it capable of dissolving quite considerable amounts of the metal. There are also some statistics of the supplies of raw material, and of production, but this division of the subject can hardly be said to exhibit equal scope and fulness of detail with the rest.

The illustrations are generally very good, the drawings large enough to be clearly intelligible, and for the most part to scale, with detail enough to serve as working drawings, while the engraver's work is very fairly done. The lettering of some of the figures is not very clear, which is always trying to the eyes in attempting to follow a description.

There are sundry useful tables, as of the indications of different hydrometers, the densities of acids, soda solutions, etc. A general index is promised to appear with the final volume of the work.

The annoyance of typographical errors has been avoided as far

* Comptes rendus, 91 : 59, 62

probably as can ever be expected in a book of so much extent and detail. Here and there a little slip of this sort may be noticed, as on p. 51 of Vol. 2, 5th line from bottom, where the word "material" should read "immaterial" The author's command of English is such as to make his pages pleasant reading, but odd turns of expression occasionally appear. Thus, in Vol. 1, on p. 38, we read of "*a furthergoing decomposition*"; on p. 39, that "*in the hot even zinc and iron already yield sulphurous acid*"; on p. 52, that "*probably the most sensitive of all reagents on nitric acid, etc., is*," and on p. 141, that "*Petrie's burner . . . . is intended to permit a totally equal combustion of the sulphur.*" The sin of German-like *over*-fullness is not often committed in this book, but traces of it are not altogether wanting. Such a statement as appears at the top of p. 18, Vol. 1, to the effect that "*even in the animal kingdom free sulphuric acid has been found, viz: in the salivary glands of several mollusks, especially of Dolium galea, which contain 2.47 per cent. free sulphuric acid, and 0.4 per cent. of free hydrochloric acid, (Boedeker and Troschel; De Luca and Pauceri,*") might surely have been omitted from a technological treatise. It is but an ungracious task however to look up such trifling blemishes as may exist in so good and able a book as the one under review; its general design and the general style in which that design has been carried out are deserving of hearty and ungrudging praise.

In laying down this work one cannot but feel regret that in the United States the manufacture of sulphuric acid has as yet attained but very moderate development, while the great industry of soda production, of so much importance in itself to the future of the nation, and involving so much of indirect consequence to the expansion of the other chemical arts, is represented by but the single factory at Natrona, employing as material the cryolite of the ice-bound Greenland coast.

J. W. M.

HANDBUCH DER ORGANISCHEN CHEMIE. Von Dr. F. BEILSTEIN, Professor der Chemie am technologischen Institute zu St. Petersburg. Erste Lieferung. Leipzig. Leopold Voss. 1880.

The idea of bringing together in one book *descriptions of every compound known to organic chemistry, with complete references to the literature of the vast subject*, is appalling. No one but a man of indomitable will and almost superhuman industry could ever seriously think of undertaking such a piece of work. Yet it has actually been accomplished by the author of the latest production in the field of organic chemistry which is described in the above title. In their time the classical works of Gerhardt and Gmelin were practically perfect, and these authors had in view exactly what Beilstein has; but these works have long since failed to furnish chemists with a satisfactory guide to the literature of organic chemistry, and, despite the large dictionaries of chemistry and the large text-

books which have appeared within the last ten years, a want has been felt for some book which should be exhaustive, as far as references to literature are concerned, and at the same time should be brought down to date. At last the desired book is begun, and, judging by an examination of the first number and by the author's well-known reputation for thoroughness, we have no hesitation in saying that it will be all he promises and all we can wish for.

Unfortunately the beginning of a book in Germany is by no means a guarantee that it will ever be finished. Witness the great treatise on organic chemistry by Kekulé, for instance, whose incomplete third volume has been lying in many a library for thirteeen years. And in seeing this first number of a German book which must necessarily be very large, our first impulse is to assume that we shall never see the end of it, or, at least, that by the time the end is reached the beginning will be gray with the dust of ages. We are hence happy to say that the publisher promises, on the basis of manuscript already on hand, to finish the "Handbuch der organischen Chemie" in but little more than a year. There are to be about twelve numbers of 160 pages each, and these will appear at intervals of from five to six weeks uninterruptedly until the work is completed. This will make about 2000 pages, but they are large pages and printed in small type, so that the material presented would cover at least 4000 ordinary octavo pages.

The price of the book is remarkably low, bringing it within the reach of every one who needs it. Each number costs but three marks (about 75 cts.), thus making the price of the complete work only from $9.00 to $10.00.

The time for criticizing this work has not arrived, nor is it possible for one man to subject it to criticism from the only legitimate standpoint. The main question to be answered is whether the book is what its author claims it to be. Is it exhaustive? This can only be answered in the future by special investigators who have had occasion to use it as a book of reference. We have every reason to believe, however, that it will be found a thoroughly trustworthy guide to the original sources, and, as such, it will be of incalculable value to the earnest student and investigator. I. R.

Some Recent Investigations in Physical Chemisty.

Within the last few months there have appeared in the chemical journals some articles in the field of physical chemistry of much more than ordinary interest and importance The first of these to which we would call attention is by Julius Thomsen. It is entitled "*Thermochemical Investigations on the Theory of Carbon Compounds.*"* Thomsen first gives the figures obtained by him for the heats of combustion of marsh gas, CH_4, ethane, C_2H_6, pro-

* Ber. d. deutsch. chem. Gesell. 13, 1321.

pane, C_3H_8, ethylene, C_2H_4, propylene, C_3H_6, and acetylene, C_2H_2. From these experimental data he calculates by well-known methods the heats of formation of these compounds.

The results are given in the table below:

Hydrocarbon.	Molecule.	Heat of Formation.
Methane	CH_4	19570 c
Ethane	C_2H_6	24510 c
Propane	C_3H_8	29950 c
Ethylene	C_2H_4	— 4740 c
Propylene	C_3H_6	— 400 c
Acetylene	C_2H_2	—48290 c

From these figures we see how much heat is developed: (1) when two atoms of hydrogen combine with two atoms of carbon; (2) when four; (3) when six; and (4) when eight atoms of hydrogen combine with two atoms of carbon. We have:

	Difference.
C_2+H_2 —48290 c	
	550 c
C_2+H_4 — 4740 c	
	29259 c
C_2+H_6 +24510 c	
	14630 c
C_2+H_8 +39140 c	

The differences, it will be observed, are multiples of a constant, about 14600, and stand in the relation 3 : 2 : 1. If the regularity here observed be of general application, then we can complete the above table by the member C≡C, and the heat of formation of such a molecule of gaseous carbon would be —106630 c. Calling this value a, we have:

Compound to be formed.	Heat of Formation.	Diff.
C≡C	$-a$	
		$4r$
HC≡CH	$-a+4r$	
		$3r$
H_2C=CH_2	$-a+7r$	
		$2r$
H_3C—CH_3	$-a+9r$	
		r
H_4C : CH_4	$-a+10r$	

The most probable values for the two constants a and r are

$$a=106630 \text{ c.} \quad r=14573 \text{ c.}$$

The gasification heat of carbon, *i. e.* that quantity of heat which is necessary to transform two atoms of amorphous carbon into the normal gaseous condition and to form the molecule C≡C, amounts to 106630 c.

The signification of the constant r requires further examination. We may regard the gasification heat of carbon as made up of two factors: (1) the heat of dissociation of two atoms of carbon, *i. e.* that quantity of heat which is necessary to put two atoms of amor-

phous carbon in the gaseous condition *as separated atoms;* (2) the heat tonality which results when two such atoms unite by means of four bonds to form a molecule of normal gaseous carbon. Let us call the first quantity $2d$, the latter C≡C or v_4, then we have

$$-a = -2d + v_4 = -106630 \text{ c.}$$

Further, when the separated carbon atoms unite with hydrogen, three processes are to be distinguished: (1) the hydrogen molecule is dissociated by the use of an amount of heat which we may designate by $-hh$; (2) these free hydrogen atoms unite with carbon with an evolution of heat $2ch$; (3) the carbon atoms unite with each other by one, two or three bonds; the single, double and triple union may be designated by v_1, v_2 and v_3.

The formation of acetylene may be represented thus:

$$HC{\equiv}CH{=}(C_2,H_2) = -2d + v_3 + 2ch - hh.$$

Assuming that, whenever hydrogen unites with carbon to form hydrocarbons, the same heat tonality results from equal numbers of atoms, and making $2ch - hh = 2q$, we have:

C≡C	$-a$			=	$-2d + v_4$
HC≡CH	$-a$	+	$4r$	=	$-2d + v_3 + 2q$
$H_2C{=}CH_2$	$-a$	+	$7r$	=	$-2d + v_2 + 4q$
$H_3C{-}CH_3$	$-a$	+	$9r$	=	$-2d + v_1 + 6q$
$H_4C : CH_4$	$-a$	+	$10r$	=	$-2d + \ldots + 8q$

and subtracting each succeeding equation from the preceding we have further:

$$\begin{aligned} v_4 - v_3 &= 2q - 4r \\ v_3 - v_2 &= 2q - 3r \\ v_2 - v_1 &= 2q - 2r \\ v_1 &= 2q - r. \end{aligned}$$

These equations indicate the possibility of determining the values of v_4, v_3, v_2 and v_1, but other determinations are necessary before these equations can be solved.

The heats of combustion of carbon and its two oxides (C,O), (CO,O) and (C,O_2) are known, the last two being determined directly, and the first one being the difference between them. The values found by Thomsen are included in the subjoined table:

Reaction.	Heat evolved.
(C,O)	28880 c
(CO,O)	68080 c
(C,O_2)	96960 c

Now, operating as above with the hydrocarbons, let $-2d$ represent the heat of dissociation of a molecule of carbon; $-oo$ the heat of dissociation of a molecule of oxygen; co the heat of combination

of one atom of carbon and one atom of oxygen; and *oco* the heat of combination of one atom of carbon with two atoms of oxygen; then we have

$$\begin{aligned} 2(C,O) &= -2d - oo + 2co, \\ (C,O_2) &= -d - oo + oco, \end{aligned}$$

and subtracting one equation from the other,

$$(C,O_2) - 2(C,O) = d - 2co + oco = 39200 \text{ c.}$$

If the same amount of heat is evolved when two atoms of oxygen unite with two separate carbon atoms, and when they unite with one carbon atom, or, if $2co = oco$, then $-2co + oco = 0$, and it follows that $d = 39200$ c. But it may be that $2co$ is not equal to oco, then we should have $d = 39200 \text{ c} + x$.

From the values thus deduced for a, r and d, the equation

$$2(C,H_4) = -2d + 8q = -a + 10r$$

gives

$$q = 14687\text{c} + \frac{x}{4}.$$

But $q = ch - \frac{hh}{2}$, according to the above, hence

$$ch = 14687\text{c} + \frac{hh}{2} + \frac{x}{4}.$$

Now turning again to the equations given above, viz.:

$C \equiv C$	$-a$			$= -106630$ c	$= -2d + v_4$	
$HC \equiv CH$	$-a$	$+ 4r$	$=$	$- 48338$ c	$= -2d + v_3$	$+ 2q$
$H_2C = CH_2$	$-a$	$+ 7r$	$=$	$- 4619$ c	$= -2d + v_2$	$+ 4q$
$H_3C - CH_3$	$-a$	$+ 9r$	$=$	$+ 24527$ c	$= -2d + v_1$	$+ 6q$
$H_4C \vdots CH_4$	$-a$	$+ 10r$	$=$	$+ 39100$ c	$= -2d$	$+ 8q$

and inserting for d and q the values just obtained, we have

$$\begin{aligned} v_4 = c \equiv\!\!\equiv c &= -28230\text{c} + 2x \\ v_3 = c \equiv c &= + 688\text{c} + \tfrac{3}{2}x \\ v_2 = c = c &= +15033\text{c} + x \\ v_1 = c - c &= +14805\text{c} + \tfrac{1}{2}x. \end{aligned}$$

The values found for q, r and ch are then

$$\begin{aligned} q &= 14687\text{c} + \frac{x}{4} \\ r &= 14570\text{c} \\ ch &= 14687\text{c} + \frac{hh}{2} + \frac{x}{4}. \end{aligned}$$

On examining the values for v_4, v_3, v_2 and v_1 the same constant is seen to play a part in these as in the values for q, ch and r. The

constant is practically identical with r, from which follow the expressions,

$$q = r + \frac{x}{4}$$
$$v_1 = r + \frac{x}{2}$$
$$v_2 = r + x$$
$$v_3 = o + \tfrac{3}{2}x$$
$$v_4 = -2r + 2x$$

The most probable value for d is 39200 c+x. With the results thus far reached it is possible to calculate the heat of formation of any hydrocarbon $C_n H_{2m}$. The general formula is

$$(C_n, H_{2m}) = -nd + 2mq + \Sigma v,$$

in which Σv is the sum of the values for v_3, v_2, and v_1, which occur in the compound. A table is then given in which it is shown that the calculated and found values for the heat of formation of the hydrocarbons thus far experimented upon agree very closely. If the accuracy of the general formulas be conceded, then we have a new method in our possession for determining the constitution of hydrocarbons, a method, however, which is only applicable for the purpose of distinguishing between cases in which double or triple union of carbon atoms may occur.

To illustrate the application of the method, the case of benzene, C_6H_6, may be cited. If Kekulé's formula for this body is correct, its heat of formation, according to Thomsen's principle, should be

$$-6d + 6q + 3v_1 + 3v_2 = -60360 \text{ c.}$$

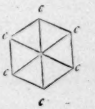
If there were no double union in benzene the heat of formation should be

$$-6d + 6q + 9v_1 = -16650 \text{ c.}$$

These values for the heat of formation correspond to the following values for the heat of combustion:

For 3 single and 3 double unions, 846040 c.
For 9 single unions, 802330 c.

The heat of combustion found by Thomsen* for benzene is 805800 c, hence he concludes that Kekulé's formula is not correct. The simplest formula which can be devised for benzene on the basis of nine single unions between carbon atoms is that in which each carbon atom is united with three others as represented thus:



* Ber. d. deutsch. chem. Gesell. 13, 1806.

A second investigation of importance is by J. W. BRÜHL, entitled "*The Chemical Constitution of Organic Bodies in Relation to their Density and their Power to Transmit Light.*"* This investigation was carried out in the laboratory which is under the direction of Prof. H. Landolt, and is characterized by great fullness and evidences of accuracy. A great many liquids have been examined by the author with reference to their refracting power, and he has succeeded in establishing important relations between this power and the constitution of the bodies.

In order to have results that can be compared with one another, the *refraction-equivalent* is determined. This is represented by the expression $P(\frac{n-1}{d})$, in which P is the molecular weight. n the index of refraction, and d the density of the body. The index is determined for four different lines of the spectrum obtained from the sodium light and from the light emitted by hydrogen in a Geissler's tube. As regards the interesting and important details of the paper, reference must be made to the original, which will well repay careful study. Here only the main results of the investigation will be summed up as briefly as possible.

Landolt has shown that, in general, bodies of the same composition have the same refraction-equivalent, the value of this equivalent being dependent upon the number and kinds of atoms present in a molecule, rather than upon the arrangement of these atoms. Each atom must then have its own refraction-equivalent, and, if we know what this is, we can calculate the equivalent for any given compound. In order to determine these quantities for carbon, hydrogen and oxygen, Landolt adopted different methods, only one of which need here be referred to. Two compounds were compared with each other, the compositions of which differed by one atom of carbon, two atoms of hydrogen or one of oxygen, and the difference in the molecular refraction of the two bodies gave the refractive power of the elements.

	$P(\frac{n-1}{d})$	Diff.
Difference in Composition C_1.		
Methyl alcohol, CH_4O	13.17	5.41
Aldehyde, C_2H_4O	18.58	
Difference in Composition H_2.		
Aldehyde, C_2H_4O	18.58	2.12
Ethyl Alcohol, C_2H_6O	20.70	
Difference in Composition O_1.		
Aldehyde, C_2H_4O	18.58	2.53
Acetic Acid, $C_2H_4O_2$	21.11	

As the mean of a large number of experiments the following values were obtained for the atomic refraction of the three elements:

$$C=5;\ H=1.3;\ O=3.$$

* Ann. der Chemie, 200, 139; 203, 1, 255, 363.

By means of these figures, then, we can calculate the refraction-equivalent of any given body composed of these three elements. On comparing the calculated values with those determined by experiment, the two are indeed found to be equal in a large number of cases, but at the same time, it is evident, in a number of other cases, that the values found by experiment are greater than those calculated. More careful examination of the subject shows that all the bodies which form exceptions to the general rule belong to the class of unsaturated compounds; and that all saturated compounds give results in harmony with the rule.

With great precautions the author has subjected a large number of pure liquid organic compounds to investigation. He has determined especially the density and the indices of refraction, and from these obtained the refraction-equivalents. A study of the results shows that the increased molecular-refraction noticed in connection with unsaturated compounds is proportional to the number of double unions between carbon atoms found in the compounds. For one double union the molecular-refraction is increased by two, for two there is an increase of four, and for three an increase of six. The law is thus stated by the author:

The excess of the molecular-refraction of bodies over the value calculated from the chemical formula is proportional to the number of carbon double unions found in the body, and, when the number of these is z, the excess amounts to z.2.

$$M = P\left(\frac{n-1}{d}\right) = R + z.2.$$

In this formula M is the refraction-equivalent actually observed, and R is the calculated value.

This law represents the principal result of the investigation, though many other results of interest are discussed in the paper.

It is shown, for instance, that:

Univalent elements have a constant atomic refraction.

The results of the investigation enable us to determine the constitution of many organic substances. Illustrations are given of the application of the principle for this purpose. It is curious to note that Brühl proves the correctness of Kekulé's formula for benzene, while Thomsen proves its incorrectness, a paradoxical state of things which requires further examination.

In continuing his work Brühl has, further, shown that there is a difference between the atomic refraction of oxygen when it is combined as in carbonyl, C=O, and when it is combined as in hydroxyl, C—O—H, a result which is of value in connection with the determination of the structure of such compounds as contain oxygen.

Finally, the author discusses the general relations existing between the constitution and physical properties of bodies. It would lead too far to go into details in regard to this part of the paper, but a few statements may be made which will serve to give an idea of the subject-matter.

It is shown that *the boiling points, densities and indices of refraction vary in the same way; that for isomeric bodies the constants of that one are largest which consists of an uninterrupted chain of hydrocarbon residues, and that the constants become smaller the more the structure of the molecule is branched and deviates from one direction.*

The data thus far established seem also to show that the shorter the molecule of isomeric bodies, *i. e.* the more they approach the spherical form, the larger is the molecular volume.

The words "shorter," "branched," etc., used in the above statements have primarily, of course, reference to the appearance of the formulas in common use which are not supposed to represent the arrangement of the atoms in space. But assuming that these formulas do in a crude way represent the actual shapes of the molecules, it is shown that there probably exists a direct connection between the variations in the physical constants of isomeric bodies and the actual shape of their molecules.

Thus the specific gravity of bodies with long molecules would necessarily be greater than that of bodies with branched or spherical molecules, for the same reason that we can get more rods in a given space than spheres of the same weight.

So also with reference to the boiling point. The rod-shaped molecules offer the most points of contact, the spherical the least. The adhesion between molecules of the first kind will hence be the greatest, and the passage of the body into the form of vapor will be more difficult than is the case with other bodies, or the boiling point will be higher. Similar considerations indicate that the facts observed in connection with the time of transpiration of vapors are in harmony with the view that the usual formulas actually represent the shapes of molecules.

Two further papers have appeared, the results of which are of importance to the subject treated in Brühl's memoir. These are: 1st. "*On the relation between the molecular weights of substances and their specific gravities when in the liquid state*," by T. E. Thorpe;* and 2d. "*On the time of transpiration of vapors*," by R. Pribram and A. Handl.† Space will not permit, however, more than a simple reference to these papers. They both appear to be models of accurate investigation and both have led to important results. They are to be continued, and we may look for further developments of interest. The amount of pains-taking labor involved in all the investigations here referred to is enormous, and the authors certainly deserve great credit for the work they have done. I. R.

* Journal of the Chemical Society (London), 1880, pp. 141, 189, 327, 341.
† Sitzungsberichte der Wiener Akad. der Wissensch. 80, 17.

THE ATOMIC THEORY. By Ad. Wurtz, Membre de l'Institut; Doyen Honoraire de la Faculté de Médecine; Professeur à la Faculté des Sciences de Paris. Translated by E. Cleminshaw, M. A., F. C. S., F. I. C., Assistant-Master at Sherborne School. C. Kegan Paul & Co., 1 Paternoster Square, London. 1880.

It is a peculiar fact that in France, which is frequently claimed as the birth-place of chemistry, and where many of the important advances which have led to the development of what is called "modern chemistry" have undoubtedly been made, there should exist to-day a strong feeling among a class of prominent chemists in opposition to the very foundation of modern chemistry, the atomic theory. It is to this fact perhaps that we owe, at least partially, the book which forms the subject of this notice. The writer of the book, M. Wurtz, has taken upon himself the championship of the atomic theory in opposition to the severe censures of the conservative school which is headed by Berthelot and St. Claire-Deville, and for some time past an interesting discussion has been carried on in the pages of French scientific journals, in which the above-named chemists have taken most prominent part.

The book before us may be regarded as a summing up of the case for the atomic theory. As it is written ostensibly for popular reading, it deals as little with purely technical matters as the nature of the subject will permit, though we doubt whether any one but a chemist fairly well trained in his subject could read it understandingly. In general it is clear and logical, and its study will be of benefit to the earnest student of chemical philosophy. It is true that the author here and there gives evidences of his position as advocate in the case, and allows his feeling of partisanship to show itself. In the first part of the book, which has to deal with the earlier stages of the historical development of the subject, this is not so noticeable, but in the chapters upon Atomicity, Affinity and the Constitution of Bodies it is certainly a defect.

The work is divided into two parts, Book I treating of Atoms, and Book II of Atomicity.

There is scarcely anything to be said save in commendation of the first part of the book. It contains very little that is new, and, in the estimate which the writer places upon the value of the investigations discussed, he agrees with most others who have treated the subject, as Kopp, Ladenburg and Lothar Meyer. A full and clear exposition of the views of Mendelejeff is given and the *periodic law* is enthusiastically spoken of. As regards this part of the subject, a serious disagreement has arisen between Lothar Meyer and Wurtz, the former claiming that sufficient credit has not been given him in connection with the relations between the atomic weights and the properties of the elements. Public letters on the subject have been exchanged, and finally Mendelejeff has expressed himself in no ambiguous terms in reply to Meyer. The discussion is still open and at present stands about in this way: Wurtz gives Mendelejeff almost the entire credit for the discovery

of the great periodic law, and Mendelejeff agrees with Wurtz in his view of the subject. Lothar Meyer, on the other hand, regards himself as the real discoverer of the law, or rather as one whose labors have done a great deal to perfect it.

Special attention is called to the relation which exists between the atomic weights and the power of bodies of emitting luminous rays, as described by Lecoq de Boisbaudran. This chemist "has proved that, for analogous elements, such as potassium, rubidium and cæsium; calcium, strontium and barium; aluminium, gallium and indium, the increase of atomic weight is proportional to the increase of wave-length, which corresponds with the spectral lines of each of these metals."

In treating of atomicity the author has hardly succeeded in throwing new light upon this intricate subject. He first shows how the present view regarding the property of atomicity had its origin in the early recognition of "the unequal saturating capacity possessed by bases for acids, and the unequal saturating capacity possessed by acids for bases;" how from this origin came the distinction between radicals of different basicity and the idea of types. Then came the researches of Frankland on organo-metallic bodies, and in a paper published in 1852 (not 1872 as is erroneously stated) this chemist first "called attention to the power which metals possess of combining with a fixed and definite number of atoms."

The development of the idea of atomicity is clearly set forth, indeed we do not recall a better treatise on this subject. But coming down to the present, the author is of course brought face to face with the same difficulties which other writers have encountered, and we think he has not been more successful than others in overcoming them. That there is a property of atoms, or of matter, which is somewhat vaguely designated by the term atomicity, very few will be inclined to doubt, but when it comes to giving a definition of this property, the accurate thinker must necessarily, in the present state of our knowledge, be puzzled. There are serious objections to considering atomicity as a fixed property, and there are also some objections to the opposite view, viz., that it is a variable property. M. Wurtz wisely adopts an intermediate course, stating that atomicity is a relative property of atoms, *i. e.* the atomicity of any given atom is determined, to some extent, by the nature of the atom or atoms with which it enters into combination. There is undoubtedly a germ of truth in this view of the matter, but it does not end the difficulties; for, even granting that any given element is trivalent towards one element and quinquivalent towards a second, it cannot be claimed that these relations are fixed. Take the case of phosphorus for example. This element is said to be trivalent towards hydrogen and quinquivalent towards chlorine. But we know that phosphorus also acts as a trivalent element towards chlorine, as is clearly shown in the compound PCl_3. If, then, phosphorus may act as trivalent and quinquivalent

towards chlorine, why may there not be conditions under which it may act as quinquivalent towards hydrogen? And then what basis is there for the statement that phosphorus is trivalent towards hydrogen and quinquivalent towards chlorine? A similar line of thought applied in other cases shows that this idea of relative atomicity, attractive as it may at first appear, really helps us very little, if any, in a thorough comprehension of the general nature of atomicity, and it certainly does not enable us to give a clear and accurate definition of the property.

In the chapter on Constitution of Compounds the impression is left on the mind of the reader that the constitution of bodies is determined mainly by the aid of the idea of atomicity. It is true that the constitutional formulas now in use are based upon the mutual saturating power of atoms, but a formula which is not deduced from facts established by experiment, and which is simply constructed in such a way as to satisfy the hypothetical bonds of the atoms, is not of much value, and cannot be of much value, until our conceptions of atomicity are much clearer than they are at present. By way of illustrating the force of this remark, we may take the case of alcohol. The structural formula now used for this compound, viz., C_2H_5—O—H, is chiefly valuable as an expression of facts. It points out that one hydrogen atom in alcohol differs from the others, and that it is intimately associated, if not united directly, with the oxygen atom. These are facts, or at least they are the simplest interpretations of reactions actually observed. And we have a right to demand that every formula used shall, in a similar way, be an expression of facts established. By far too many of the formulas found in books are, however, simply the results of attempts to account for the atomicities of the atoms which form the constituents of the compounds represented. It is in the highest degree probable that the time will come when, given the conditions under which a compound exists, we shall be able to state with a considerable degree of certainty how the atoms are combined in the compound; but that time has not yet come, and before it comes the general nature of atomicity must necessarily be investigated much more thoroughly than it has yet been, and our ideas concerning it must become much more definite.

I. R.

NOTES.

The Opium Alkaloids.

The connection between the alkaloids from Peruvian bark and the pyridine bases has been established by a number of recent investigations, to which special attention has been called in former numbers of this Journal. E. v. GERICHTEN has now shown that a similar connection probably exists between the opium alkaloids and the pyridine bases. Apophyllenic acid, a substance obtained by oxidation indirectly from narcotine and directly from cotarnine, is shown to be the methyl ester of pyridinedicarbonic acid, $C_5H_3N(CO_2H)_2$. When apophyllenic acid is heated with concentrated hydrochloric acid to a high temperature, methyl is extracted and pyridinedicarbonic acid is produced. The latter yields pyridine C_5H_5N when heated with soda-lime.—(*Ber. d. deutsch. chem. Gesell.*, 13, 1635.)

River Water.

As the result of an elaborate investigation, C. M. TIDY has reached the following conclusions:

1. That when sewage is discharged into running water, provided the primary dilution of the sewage with pure water be sufficient, after the run of a few miles, the precise distance of travel being dependent on several conditions, the removal of the whole of the organic impurity will be effected.

2. That whatever may be the actual cause of certain diseases, *i. e.* whether germs or chemical poisons, the *materies morbi* which finds its way into the river at the sewage outfall is destroyed, together with the organic impurity, after a certain flow.

E. FRANKLAND takes exception to Tidy's conclusions, reviewing the evidence on both sides very carefully, and showing that the oxidation of sewage contained in river water cannot and does not take place rapidly. He concludes, hence, that the question, "Can running water be at all times safely used for dietetic purposes a few hours or days after it has been mixed with sewage?" must be answered in the negative. The introductory paragraph of Frankland's paper is here given:—"Twelve years ago there was a general impression amongst chemists and others that polluted water quickly regained its original purity by spontaneous oxidation. This opinion had no foundation in quantitative observations; indeed, there was not a single experimental fact to support it, for the previous condition of water analysis did not permit of the quantitative investigation of organic matter dissolved in water. The impression had gained currency from the improved appearance of a polluted river after a flow of a few miles, and also from the disappearance of smell and blackness from putrescent water under similar circumstances. Two

classes of persons, strongly interested in its acceptance, were chiefly instrumental in the origination and diffusion of this opinion. These were, first, polluters of running water; and, secondly, water companies drawing their supplies below the sewer outfalls of towns. Both these influential classes, with enormous interests at stake, have always contended that even the most abominable of organic rubbish is destroyed by oxidation, in fact utterly 'burnt up,' during a flow of a few miles. There being no similarly organized opposition to the notion, the extensive credence which it gained from those who did not care much to investigate its truth, is not surprising. It was a comfortable doctrine, and therefore a popular one. Nevertheless it did not pass entirely unchallenged; indeed, it is difficult to imagine how any chemist, accustomed to the habits of organic compounds, could accept such an opinion without the most conclusive proofs of its correctness."—(*Jour. Chem. Soc.*, May and July, 1880.)

Two Remarkable Cases of Metamerism.

LUDWIG SCHREINER has just announced a discovery of the highest importance. He has shown that, when ethyl chlorocarbonate, $CO\begin{smallmatrix}/\,Cl\\ \backslash\,OC_2H_5\end{smallmatrix}$, is allowed to act upon a solution of sodium methylate $CH_3.ONa$, a compound is formed of the formula $CO\begin{smallmatrix}/\,OCH_3\\ \backslash\,OC_2H_5\end{smallmatrix}$ which he calls *ethyl methylocarbonate*, the properties of which are well defined. If now methyl chlorocarbonate, $CO\begin{smallmatrix}/\,Cl\\ \backslash\,OCH_3\end{smallmatrix}$, be allowed to act upon sodium ethylate $C_2H_5.ONa$, a compound of the same empirical formula as that above mentioned is obtained, but the two differ markedly in their properties. This second product is called *methyl ethylocarbonate*, and its formula is $CO\begin{smallmatrix}/\,OC_2H_5\\ \backslash\,OCH_3\end{smallmatrix}$. The first product has the specific gravity 1.0372 and boils at 104°, the second has the specific gravity 1.0016 and boils at 115.5°.

In a similar way the author has succeeded in preparing two methyl-ethyl-ureas. For this purpose the compound, $CO\begin{smallmatrix}/\,NH.C_2H_5\\ \backslash\,OC_2H_5\end{smallmatrix}$, was treated with methylamine, and was thus converted into ethyl-methyl-urea, $CO\begin{smallmatrix}/\,NH.C_2H_5\\ \backslash\,NH.CH_3\end{smallmatrix}$, a body fusing at 105°; and, on the other hand, by treating the body $CO\begin{smallmatrix}/\,NH.CH_3\\ \backslash\,OC_2H_5\end{smallmatrix}$ with ethylamine

the product has the same formula as the ethyl-methyl-urea first obtained, but it has not the same properties. It fuses at 75° and does not crystallize as well.

If the results obtained by Schreiner should be verified by continued investigation, it is difficult to see how the now commonly accepted idea of the equivalence of the four affinities of the carbon atom can be maintained. — (*Journal für prak. Chemie, N. F.* 22, 353.)

The Atomic Weight of Glucinum.

Nilson and Pettersson have recently determined the specific heat of glucinum at different temperatures and conclude from their experiments that its atomic weight should be changed to 13.65. If this is really the atomic weight of glucinum, then it is impossible to include it in the table of Mendelejeff, or, at least, the place to which it would be assigned in the table would not be in harmony with its properties. LOTHAR MEYER has now taken the results of Nilson and Pettersson and shown that their conclusion is not justified, that their results correctly interpreted lead to the confirmation of the commonly accepted atomic weight for glucinum, viz. 9.10.—(*Ber. d. deutsch. chem. Gesell.* 13, 1780.)

On the Nature of Caucasian Petroleum.

Recent investigations on the petroleum found in such enormous quantities in the Caucasus have shown that it has an illuminating power about 10 per cent. greater than American petroleum, and that, in spite of its higher specific gravity, it is drawn up by lamp wicks better than the American oils. F. BEILSTEIN and A. KURBATOW have undertaken a chemical examination of the more volatile portions of the crude petroleum, and have found that they consist mainly of the hydrogen addition-products of the aromatic hydrocarbons C_nH_{2n-6}. These hydrocarbons have been thoroughly investigated by Wreden. On comparing the substances from Caucasian petroleum with those described by Wreden the identity was established. The best known members of the series are: Hexahydrobenzene, C_6H_{12}; hexahydrotoluene, C_7H_{14}; and hexahydroxylene, C_8H_{16}.—(*Ber. d. deutsch. chem. Gesell.* 13, 1818.)

NOTE.—A complete list of publications relating to chemistry from the time of the last list to the present will be given in the next number.

ERRATUM.

The numeral VI. in connection with the title p. 305 should refer to the general title "On the Ethers of Uric Acid."